Synthesis, Crystal Structure and Luminescence Properties of a Cyclometalated Ir(III) Complex of 3,4-Diphenylcinnoline

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Z. Naturforsch. **2010**, *65b,* 511 – 515; received November 26, 2009 / revised February 1, 2010

An iridium(III) complex, [(dpci–H)$_2$Ir(dafo)](PF$_6$) (dpci–H = deprotonated 3,4-diphenylcinnoline, dpci; dafo = 4,5-diazafluoren-9-one), was synthesized from the reaction of the iridium complex [Ir(dpci–H)$_2$(Cl)]$_2$ and dafo in methanol, and characterized by single-crystal X-ray diffraction along with FT-IR, UV/Vis, ^{1}H NMR and mass spectroscopy. The luminescence properties and the decay of the cyclometalated iridium(III) complex were also investigated. Excitation at the absorption wavelength (469 nm) resulted in a strong emission band centered at 591 nm with a lifetime of 0.9 μs.

Key words: Iridium(III) Complex, 3-Phenylcinnoline, Crystal Structure, Photoluminescence

Introduction

Cyclometalated Ir(III) complexes belong to the family of organometallic triplet emitters, which are of great interest because of their application in electroluminescent devices and sensors [1, 2]. Owing to the strong spin-orbital mixing of heavy metal ions in phosphorescent complexes, both singlet and triplet excitons can be fully utilized, creating the possibility for electrophosphorescent dye-doped devices to reach an internal quantum efficiency of 100 % [3]. Iridium(III) complexes are highly tunable over the entire visible and near-infrared (NIR) region, generally with relatively small changes in the coordinating ligands, and are commonly used in electroluminescent applications due to their excellent redox properties. Light-emitting devices doped with iridium complexes have achieved nearly 100 % internal phosphorescence efficiency in the green and red emissions [4]. At the same time, Ir(III) complexes are promising candidates in various sensor applications on account of their intense emission, wide range of emission energies, long-lived emitting states and high luminescence quantum yields. They have successfully been explored as phosphorescent chemosensors for anions, oxygen concentration, and metal ions. Iridium(III) complexes have also been developed as biological labeling reagents, which show high sensitivity upon binding to avidin [5] and protein [6].

Recently, we have reported a red emitting device, using phenyl-phthalazine iridium(III) complexes as dopants by a solution process, with an internal quantum efficiency of nearly 100 % [7]. Mi *et al.* reported efficient and thermally stable OLEDs using diphenylphthalazine iridium(III) [8]. Based on this work, it has been found that the ligands with an *sp*^{2}-hybridized N atom adjacent to the chelating N atom, such as phenylpyridazine and phenylphthalazine derivatives [1], are beneficial for the iridium(III) complexes due to the shorter bond length and the stronger bonding strength between the chelating N atom and the Ir atom, compared with analogs which have a C atom instead of the non-chelating N atom. In one of our studies, cinnoline derivatives as another type of isomers of benzopyridazine besides phthalazine were now used to synthesize a novel cyclometalated Ir(III) complex, [(dpci–H)$_2$Ir(dafo)](PF$_6$) (dpci–H = deprotonated 3,4-diphenylcinnoline, dpci; dafo = 4,5-diazafluoren-9-one). The structural chacterization and photoluminescence properties are also reported in this paper.

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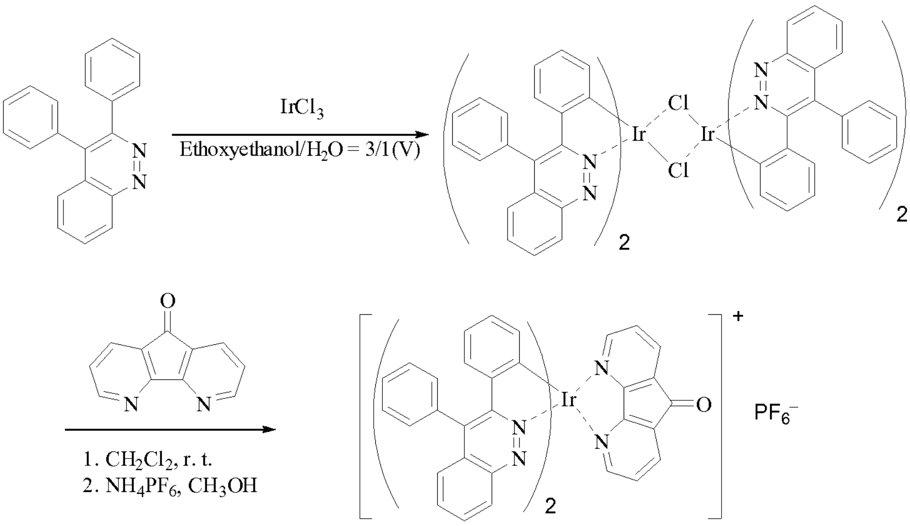

Scheme 1. Synthetic route to [Ir(dpci–H)$_2$(dafo)][PF$_6$].

Experimental Section

General

The solvents were purified by routine procedures and distilled under an atmosphere of dry nitrogen before use. All reagents, unless otherwise specified, were purchased from Aldrich and were used as received. 3,4-Diphenylcinnoline and 4,5-diazafluoren-9-one were prepared according to procedures described in the literature [9, 10]. The infrared spectrum was recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. UV/Vis absorption spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. Positive-ion ESI mass spectra were recorded on a Perkin Elmer Sciex API 365 mass spectrometer. ^{1}H NMR spectra were recorded on a Varian Inova500NB spectrometer using CDCl$_3$ as solvent. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Luminescence lifetime was determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument.

*Synthesis of [Ir(dpci–H)$_2$(dafo)]PF$_6$ (**1**)*

The synthetic route to [Ir(dpci–H)$_2$(dafo)]PF$_6$ is given in Scheme 1.

To a round-bottomed flask (25 mL), 2-ethoxyethanol (9 mL), 3,4-diphenylcinnoline (0.5 g, 2.0 mmol), IrCl$_3$·3H$_2$O (0.2 g, 0.56 mmol) and water (3 mL) were added sequentially. The mixture was stirred under nitrogen at 120 °C for 24 h and then cooled to r. t. The precipitate was collected and washed with ethanol and acetone, and then dried in vacuum to give a dark-red cyclometallated Ir$^{\text{III}}$-μ-chloro-bridged dimer (0.36 g).

In a round-bottomed flask, 0.05 g of this dichloro-bridged iridium dimer and 0.02 g of 4,5-diazafluoren-9-one were mixed together in 10 mL of methanol. The solution was then refluxed overnight under an inert atmosphere. After cooling to r. t., counterion exchange from Cl$^-$ to PF$_6{}^-$ was accomplished *via* a metathesis reaction in which the product was precipitated from the methanol solution with an excess of NH$_4$PF$_6$, washed with water and methanol, and dried. Orange-red crystals of [Ir(dpci–H)$_2$(dafo)]PF$_6$ (**1**) were obtained from column chromatography using CH$_2$Cl$_2$ and acetone (10:1) and repeated recrystallization using a mixture of CH$_2$Cl$_2$ and hexane at r. t. (0.057 g, 84 %). – IR (KBr): ν = 1632 (CO), 840 (PF$_6{}^-$) cm^{-1}. – ^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.17 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.5 Hz, 2H), 6.66 (t, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.62 (t, J = 6.0 Hz, 2H), 7.68 – 7.78 (m, 10H), 7.89 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 5.5 Hz, 2H), 8.29 (d, J = 8.5 Hz, 2H). – MS ((+)-ESI): *m/z* = 937 (calcd. 937 for {[Ir(dpci–H)$_2$(dafo)]}$^+$, [M]$^+$).

Crystal structure determination

A single crystal of **1** was mounted on a glass fiber. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK_α radiation at 296 K using an ω scan mode. The collected frames were processed with the software SAINT [11]. The data were corrected for absorption using the program SADABS [12]. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [13]. Crystal data, data collection parameters and details of the structure refinement are given in Table 1, and selected bond lengths and angles are summarized in Table 2.

Comment: The complex **1** crystallizes in the triclinic space group $P\bar{1}$ with Z = 2. While one PF$_6{}^-$ anion resides on a crystallographic center of inversion, a second one was

Table 1. Crystal data, data collection parameters and details of the structure refinement of **1**.

Complex	$[(3,4\text{-diphenylcinnoline–H})_2\text{Ir}(4,5\text{-diazafluoren-9-one})]^+\text{PF}_6^-$
Empirical formula	$C_{51}H_{32}F_6IrN_6OP$
Formula weight	1082.04
Color, habit	orange, block
Crystal size, mm^3	0.10 × 0.13 × 0.30
T, K	296(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	9.6200(4)
b, Å	15.5722(8)
c, Å	16.2099(8)
α, deg	89.612(3)
β, deg	78.681(3)
γ, deg	74.230(3)
V, Å^3	2288.67(19)
Z	2
$D_{\text{calcd.}}$, g cm^{-3}	1.57
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	3.0
$F(000)$, e	1068
Radiation; λ, Å	$\text{Mo}K_\alpha$; 0.71073
Refl. coll. / indep. / R_{int}	41658 / 10494 / 3.29
Reflections with $[I \geq 2\,\sigma(I)]$	9115
Parameters refined	598
Final $R1$ / $wR2$ indices (all data)[a]	0.0470 / 0.1213
Goodness of fit (GoF)[b]	1.082
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	1.88 / −0.73

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$ where n_{obs} is the number of data and n_{param} the number of refined parameters.

found on a general position and was refined with half occupancy. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp^3}–H = 0.96 Å) and included in the structure factor calculations with assigned isotropic displacement parameters, but were not refined.

CCDC 748661 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

$IrCl_3{\cdot}xH_2O$ and two equivalents of diphenylcinnoline were reacted in 2-ethoxyethanol/water solution under reflux condition. A dichloro-bridged dimeric iridium complex was formed. Because the dimeric complex was unstable in air, it was used directly in the following step without further purification. It dissociated readily on addition of 4,5-diazafluoren-9-one to give the title complex **1**.

Table 2. Selected bond lengths (Å) and angles (deg) for $[(3,4\text{-diphenylcinnoline-H})_2\text{Ir}(4,5\text{-diazafluoren-9-one})]^+\text{PF}_6^-$ (**1**).

Ir(1)–N(1)	2.014(4)	N(1)–N(2)	1.311(6)
Ir(1)–N(3)	2.032(4)	N(3)–N(4)	1.306(6)
Ir(1)–N(6)	2.201(5)	Ir(1)–C(20)	1.986(5)
Ir(1)–N(5)	2.210(4)	Ir(1)–C(40)	2.003(5)
O(1)–C(51)	1.203(8)		
C(20)–Ir(1)–C(40)	95.0(2)	C(20)–Ir(1)–N(6)	95.10(19)
C(20)–Ir(1)–N(1)	79.4(2)	C(40)–Ir(1)–N(6)	168.26(18)
C(40)–Ir(1)–N(1)	94.08(19)	N(1)–Ir(1)–N(6)	93.59(18)
C(20)–Ir(1)–N(3)	95.31(19)	N(3)–Ir(1)–N(6)	92.86(18)
C(40)–Ir(1)–N(3)	80.32(19)	C(20)–Ir(1)–N(5)	171.06(18)
N(1)–Ir(1)–N(3)	171.99(16)	C(40)–Ir(1)–N(5)	90.78(18)
N(1)–Ir(1)–N(5)	93.46(18)	N(2)–N(1)–Ir(1)	120.3(4)
N(3)–Ir(1)–N(5)	92.35(16)	C(14)–N(1)–Ir(1)	116.0(3)
N(6)–Ir(1)–N(5)	79.90(17)	N(1)–N(2)–C(1)	118.5(5)
N(2)–N(1)–C(14)	123.9(4)	N(4)–N(3)–C(34)	123.9(4)
N(4)–N(3)–Ir(1)	118.4(3)	C(45)–N(5)–Ir(1)	108.1(3)
C(34)–N(3)–Ir(1)	117.5(3)	C(41)–N(5)–Ir(1)	136.6(4)
N(3)–N(4)–C(21)	118.7(4)	C(46)–N(6)–C(50)	114.4(5)
C(45)–N(5)–C(41)	115.2(5)	C(46)–N(6)–Ir(1)	108.7(3)
C(50)–N(6)–Ir(1)	136.6(4)		

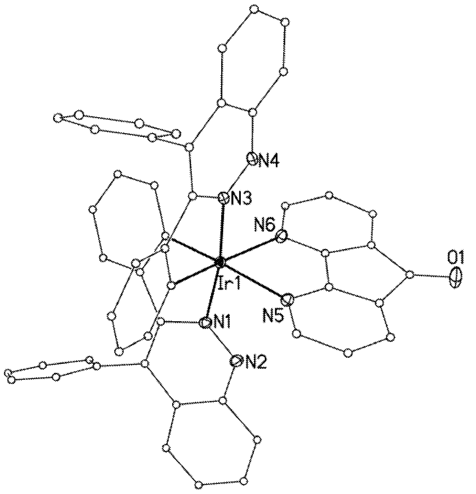

Fig. 1. Perspective view of the $[(3,4\text{-diphenylcinnoline–H})_2\text{Ir}(4,5\text{-diazafluoren-9-one})]^+$ cation with selected displacement ellipsoids drawn at the 30 % probability level, H atoms omitted.

The molecular structure of complex **1** is depicted in Fig. 1, including selected bond lengths and angles. A distorted octahedrally coordinated iridium(III) cation is ligated by two cyclometalated dpci ligands and one chelating dafo ligand with $[PF_6]^-$ as counter anion. The two dpci–H ligands chelate the iridium center with N-N in the *trans* and C-C in the *cis* configuration. The average Ir–C bond length (2.000(5) Å) is within the range reported for closely related com-

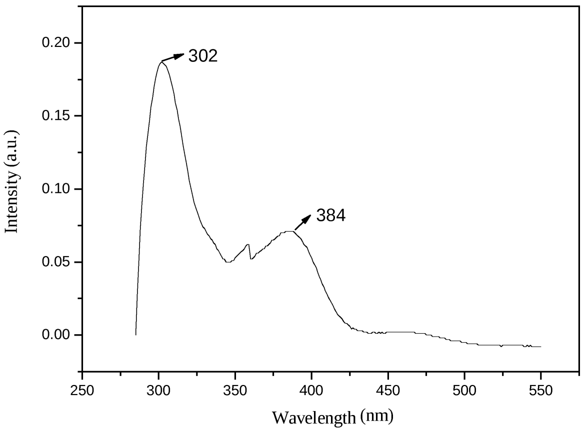

Fig. 2. UV absorption spectrum of [Ir(dpci–H)$_2$(dafo)]PF$_6$ in CH$_2$Cl$_2$.

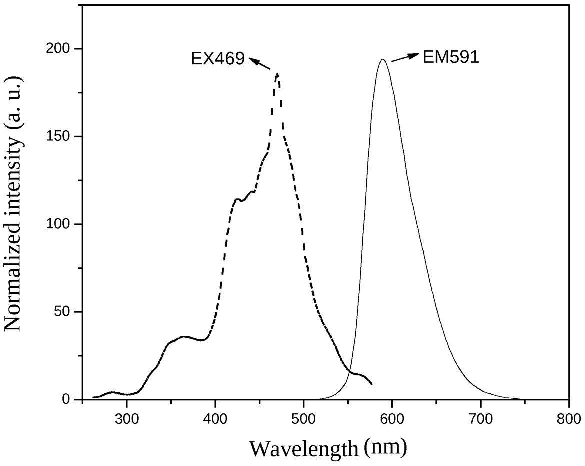

Fig. 3. Excitation and emission spectra of [Ir(dpci–H)$_2$(dafo)]PF$_6$ in CH$_2$Cl$_2$at room temperature.

plexes [14]. The Ir–N bond lengths of the dpci–H ligands (2.014(4) to 2.023(4) Å), are within the range reported for other mononuclear complexes containing analogous Ir[C$^\wedge$N] moieties [15]. Moreover, the Ir–N bond lengths between the Ir center and the dafo ancillary ligand are longer than those between the Ir center and the dpci–H ligands because of stronger donating and back-bonding interactions between the aryl groups of dpci–H and the iridium atom. The dafo chelation results in an N(5)–Ir(1)–N(6) bond angle of 79.9(17)°, appreciably smaller than the idealized 90° value. Furthermore, the C–C and C–N bond lengths and angles are within normal ranges and are in agreement with corresponding parameters described for similarly constituted complexes [16].

In the UV/Vis absorption spectrum of [Ir(dpci–H)$_2$(dafo)]PF$_6$ (Fig. 2), the absorption band around 302 nm is assigned to a typical spin-allowed $^1\pi$-π^* transition of the ligands. On the other hand, the band at 384 nm is assignable to the singlet metal-to-ligand charge transfer (^{1}MLCT). The moderately intense absorptions at *ca.* 450 – 500 nm can be assigned to a spin-forbidden triplet metal-to-ligand charge transfer (^{3}MLCT).

Fig. 3 shows the room-temperature photoluminescence spectrum of [Ir(dpci–H)$_2$(dafo)]PF$_6$ in degassed CH$_2$Cl$_2$. The excitation spectrum is dominated by a broad band centered at 468 nm, which is the absorption arising from the ^{1}MLCT and ^{3}MLCT states. The emission maximum for Ir(dpci–H)$_2$(acac) (acac = acetylacetonate) appears at 665 nm, while the emission maximum for **1** appears at 591 nm. So the complex emission is the mixture of Ir-to-(dpci–H) ^{3}MLCT, Ir-to-dafo ^{3}MLCT and includes the ligand-centered triplet (^{3}LC) state [17].

The excited state lifetime was determined to be 0.9 μs for complex **1**. In general, the radiative lifetime of the cationic iridium complexes falls in the microsecond range [18], and the experimental decay time is also in this range.

In conclusion, the new complex shows interesting photophysical properties. Investigations into and applications of the complex are currently in progress.

Supporting Information

Tables with the IR absorption spectrum, the ^{1}H NMR spectrum, and the decay curve of [Ir(dpci–H)$_2$-(dafo)]PF$_6$ are provided as Supporting Information online only (http://www.znaturforsch.com/ab/v65b/c65b.htm).

Acknowledgement

This project was supported by the National Natural Science Foundations of China (grant nos. 50903001, 50803027 and 90922008) and the Program for New Century Excellent Talents in University of China (NCET-06-0556).

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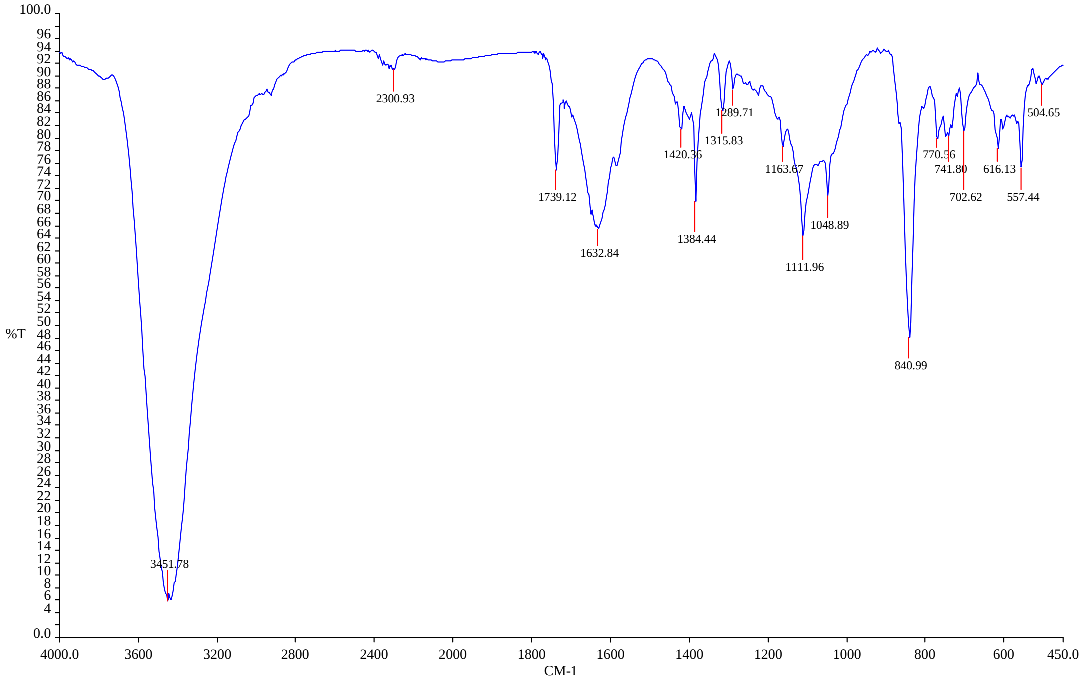
Supporting Information

Fig. S1. IR absorption spectrum of Ir(dpci–H)$_2$(dafo)PF$_6$.

Fig. S2. ^{1}H NMR spectrum of Ir(dpci–H)$_2$(dafo)PF$_6$.

Fig. S3. Decay curve of Ir(dpci–H)$_2$(dafo)PF$_6$.



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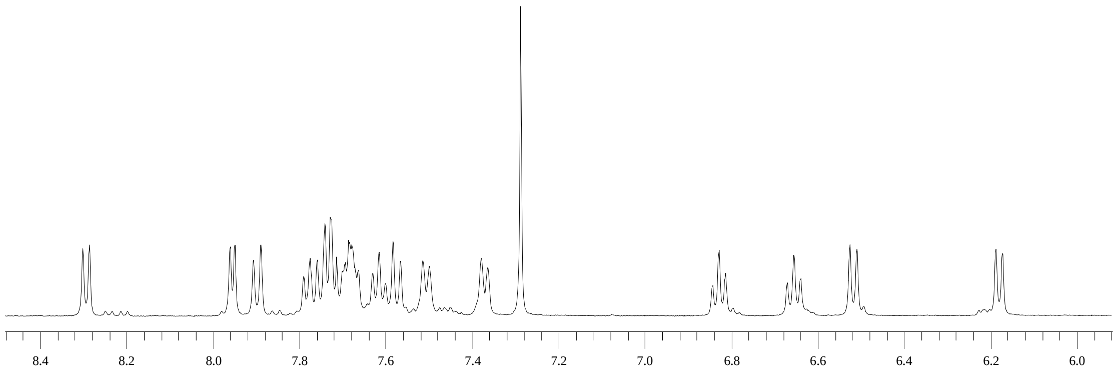

Fig. S2. ^{1}H NMR spectrum of Ir(dpci–H)$_2$(dafo)PF$_6$.

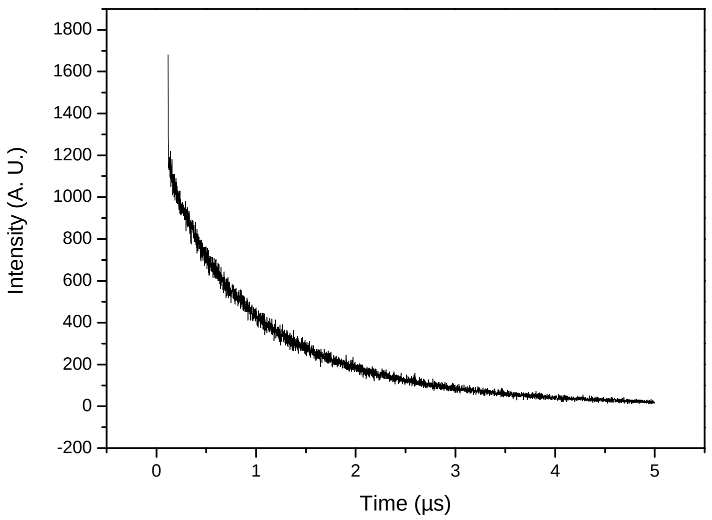

Fig. S3. Decay curve of Ir(dpci–H)$_2$(dafo)PF$_6$.