Phosphorescent Complexes

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Near-IR Phosphorescent Ruthenium(II) and Iridium(III) Perylene Bisimide Metal Complexes**

Marcus Schulze, Andreas Steffen, and Frank Würthner**

Abstract: *The phosphorescence emission of perylene bisimide derivatives has been rarely reported. Two novel ruthenium(II) and iridium(III) complexes of an azabenz-annulated perylene bisimide (ab-PBI),* $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ ***1*** *and* $[Cp^*Ir(ab\text{-}PBI)Cl]PF_6$ ***2*** *are now presented that both show NIR phosphorescence between 750–1000 nm in solution at room temperature. For an NIR emitter, the ruthenium complex* ***1*** *displays an unusually high quantum yield* (Φ_p) *of 11 % with a lifetime* (τ_p) *of 4.2 μs, while iridium complex* ***2*** *exhibits* $\Phi_p < 1\,\%$ *and* $\tau_p = 33$ *μs.* ***1*** *and* ***2*** *are the first PBI-metal complexes in which the spin–orbit coupling is strong enough to facilitate not only the* $S_n \rightarrow T_n$ *intersystem crossing of the PBI dye, but also the radiative* $T_1 \rightarrow S_0$ *transition, that is, phosphorescence.*

Perylene bisimide (PBI) dyes are well-known for their high tinctorial strength, intense fluorescence, excellent (photo)-stability, and their ability to form stable radical anions.[1] With this unique combination of optical and electronic properties they have entered many research fields, including organic electronics,[2] optical sensing,[3] single-molecule spectroscopy[4] and supramolecular photochemistry.[5] Many of these applications make use of the energetically lowest singlet excited state (S_1) of PBI. However, there are only few reports of PBI derivatives of which the triplet excited state T_1 can easily be accessed and its triplet properties be used. One example has been described by Janssen and co-workers, who investigated a cofacially stacked PBI dimer and could demonstrate triplet state formation by singlet oxygen sensitization experiments.[6] Photoexcitation of this dimer stack leads to a highly polarized charge transfer (CT) state, which accelerates the intersystem-crossing (ISC) process. Studies by Flamigni and co-workers on perylene tris-dicarboximides revealed the rare case of triplet excited state formation in monomeric perylene compounds.[7] However, the phosphorescence spectrum could only be obtained in a 77 K glass matrix by an external heavy atom effect that is mediated by ethyl iodide. Despite the achieved progress in studying the triplet state of PBI systems by indirect methods, the most obvious access to the T_1 state is by an internal heavy atom effect, which can be accomplished by introduction of a late-transition-metal center with strong spin–orbit coupling (SOC) directly in the molecule itself to facilitate ISC. Castellano and co-workers contributed to this approach several PBI-Pt conjugates with acetylene bridges, and they were able to populate the PBI intraligand triplet (^{3}IL) state with up to 55 % quantum yield.[8] Other examples of the Wasielewski group showed that attachment of either an Ir complex to the imide position of PBI or a Ru fragment to the PBI bay area leads to very fast charge separation, which is a competitive pathway due to the strong photo-oxidation properties of the dye.[9] Rybtchinski and co-workers delivered an example of a PBI with a Pd complex directly attached at the bay position, which counterintuitively has negligible influence on the PBI ^{1}IL state properties exhibiting a remarkable high fluorescence quantum yield (Φ_f) of 65 %.[10] Although access to the PBI ^{3}IL state has been achieved, phosphorescence originating from that state has apparently not been observed for PBI-based transition metal complexes.[11] Obviously, the SOC of the metal atoms used in the reported systems is not of sufficient extent for the radiative transition from T_1 to the ground state S_0, that is, phosphorescence.

Herein, we report the first examples of PBI-metal complexes $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ **1** and $[Cp^*Ir(ab\text{-}PBI)Cl]PF_6$ **2**, which show emission from their PBI ^{3}IL state even at room temperature in solution. The azabenzannulated perylene bisimides (ab-PBIs) were prepared by an optimized method[12] in three steps, starting from perylene bisanhydride, in overall yield of 30 % (for details see the Supporting Information). Afterwards, the bipyridine-like ab-PBI ligand **3a** (R^1 = 2,2-diisopropylphenyl) was reacted with $[RuCl_2(bpy)_2]$ and an excess of $AgClO_4$, and subsequent anion exchange with NH_4PF_6 afforded the complex $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ **1** in 65 % yield (Scheme 1). The iridium complex $[Cp^*Ir(ab\text{-}PBI)Cl]PF_6$ **2** was prepared by the reaction of ab-PBI **3b** (R^2 = 3-pentyl) with half an equivalent of $[Cp^*IrCl_2]_2$ and subsequent anion exchange with NH_4PF_6 in 67 % yield. Both complexes, **1** and **2**, were characterized by elemental analysis, NMR spectroscopy (Supporting Information, Figures S4–S7), MALDI-TOF and high-resolution electrospray ionization (ESI) mass spectrometry (Supporting Information, Figures S12–S15).

The molecular structure of **2** was confirmed by single-crystal X-ray diffraction studies (Figure 1). The iridium(III)

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[*] M. Schulze, Prof. Dr. F. Würthner
Universität Würzburg, Institut für Organische Chemie and
Center for Nanosystems Chemistry
Am Hubland, 97074 Würzburg (Germany)
E-mail: wuerthner@chemie.uni-wuerzburg.de

Dr. A. Steffen
Universität Würzburg, Institut für Anorganische Chemie
Am Hubland, 97074 Würzburg (Germany)
E-mail: andreas.steffen@uni-wuerzburg.de

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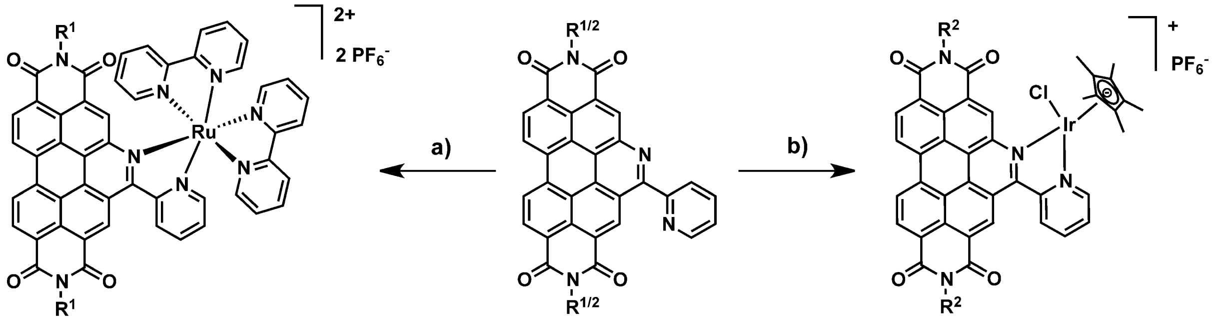

[Ru(bpy)$_2$(ab-PBI)][PF$_6$]$_2$ 1

3a: R^1 = 2,6-diisopropylphenyl
3b: R^2 = 3-pentyl

[Cp*Ir(ab-PBI)Cl]PF$_6$ 2

Scheme 1. Synthesis of complexes [Ru(bpy)$_2$(ab-PBI)][PF$_6$]$_2$ **1** and [Cp*Ir(ab-PBI)Cl]PF$_6$ **2**. Reaction conditions: a) [RuCl$_2$(bpy)$_2$], AgClO$_4$, LiCl, NEt$_3$, CHCl$_3$/EtOH 3:1, 65 °C, 48 h, Ar; NH$_4$PF$_6$, 65 %; b) [Cp*IrCl$_2$]$_2$, CHCl$_3$, 40 °C, 16 h, Ar; NH$_4$PF$_6$, 67 %.

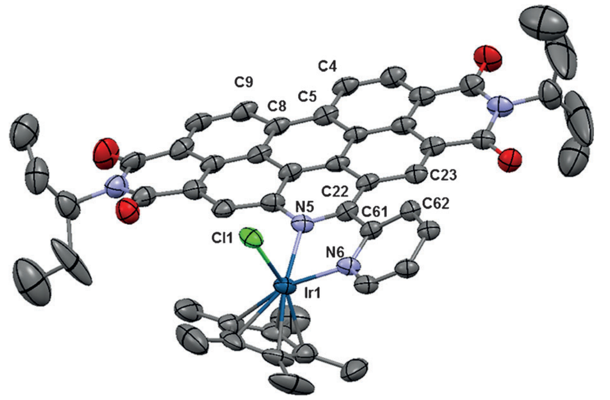

Figure 1. Molecular structure of [Cp*Ir(ab-PBI)Cl]PF$_6$ **2** in the solid state (ellipsoids set at 50 % probability; hydrogen atoms and counterion omitted for clarity).

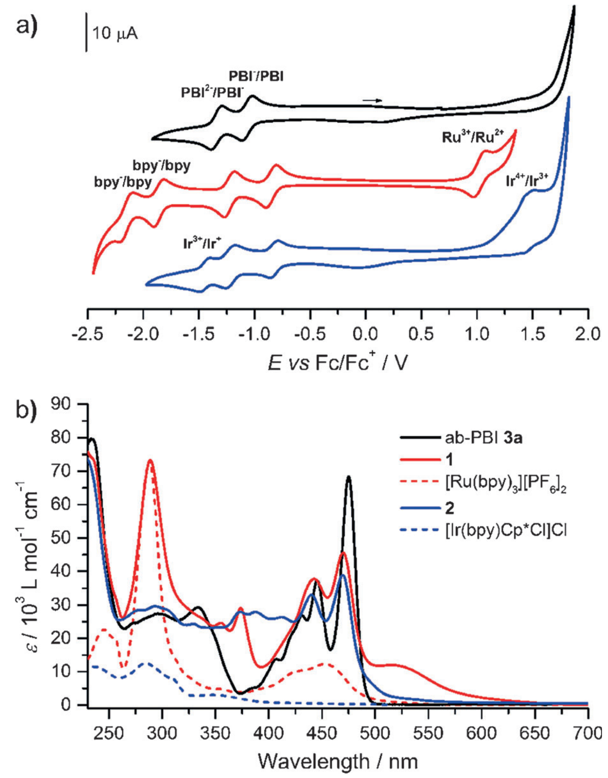

Figure 2. a) Cyclic voltammograms of ab-PBI (only **3a** shown), **1**, and **2**. The measurements were performed in dry dichloromethane at room temperature at a concentration of $2.5{\cdot}10^{-4}$ mol L^{-1} (electrolyte: 0.1 mol L^{-1} nBu$_4$NPF$_6$). The values were corrected versus ferrocene as an internal standard. b) UV/Vis spectra of ab-PBI (only **3a** shown), **1**, and **2** (along with these of corresponding references [Ru(bpy)$_3$][PF$_6$]$_2$ and [Cp*Ir(bpy)Cl]Cl,[14] dashed lines) in dichloromethane at a concentration of $1{\cdot}10^{-5}$ mol L^{-1} at room temperature.

center in **2** is coordinated in a piano-stool conformation in which the Cp* ligand occupies three of the six possible coordination sites. All bond lengths and angles of **2** are in agreement with the corresponding reference compound [Cp*Ir(bpy)Cl]Cl,[13] except the iridium(III)–nitrogen bond Ir–N5 (2.138(5) Å) and the Ir–Cp* distance (1.803(8) Å). For both, elongations compared to the reference (d(Ir–bpy) = 2.076(8)/2.090(9) and d(Ir–Cp*) = 1.786 Å) are observed and attributed to the electron-withdrawing character of the PBI moiety. Furthermore, the pyridyl ring is twisted out of the flat PBI plane (φ (C4-C5-C8-C9) = 3.80°) by 18.3° owing to the steric constraint between the C62 and C23 hydrogen atoms.

We have investigated the electrochemical properties of PBI complexes **1** and **2** by cyclic voltammetry. These studies revealed a shift of the two reversible PBI reductions PBI$^{-/0}$ and PBI$^{2-/-}$ of the free ab-PBI ligands (both ligands have identical redox potentials; see the Supporting Information, Table S1) from −1.06 V and −1.34 V *vs* Fc$^{+/0}$, respectively, to −0.85 V and −1.23 V for **1** and to −0.82 V and −1.22 V for **2** upon complexation (Figure 2a). The easier reduction of ab-PBI upon coordination to the Lewis acidic metal ion centers is accompanied by a more difficult oxidation of the metal centers in these complexes. The reversible Ru$^{3+/2+}$ redox couple appears at +1.02 V in [Ru(bpy)$_2$(ab-PBI)][PF$_6$]$_2$ **1** (+0.88 V in [Ru(bpy)$_3$]$^{2+}$)[15] and the irreversible Ir$^{4+/3+}$ oxidation in [Cp*Ir(ab-PBI)Cl]PF$_6$ **2** at +1.46 V (+1.40 V in [Cp*Ir(bpy)Cl]$^+$).[16] This redox behavior of **1** and **2** is related to the electron-withdrawing nature of the electron-poor PBI unit, which destabilizes the higher oxidized state of the metal centers.

The optical properties of the new PBI-based complexes **1** and **2** were studied by UV/Vis absorption and luminescence spectroscopy. The absorption features of the PBI ligand (**3a** and **3b**) are fairly recognizable with its strong π–π* band at about 470 nm ($\varepsilon \approx 65\,000\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) and the corresponding vibronic progressions (Figure 2b). In compound **1** and **2**, these characteristics are not changed fundamentally, except for a small 5 nm hypsochromic shift and a broadening of the fine structure. However, compound **1** shows a new additional broad absorption band at around 520 nm, which is assigned to a bathochromically shifted metal-to-ligand charge transfer (MLCT) transition, which relates to the MLCT state of $[\mathrm{Ru(bpy)_3}]^{2+}$ at 450 nm.[17] The iridium compound **2** exhibits several new bands between 370–420 nm, which are apparently arising from MLCT transitions, and thus leading to a nearly constant absorptivity from 250 to 470 nm with an extinction coefficient of about $30\,000\ \mathrm{L\,mol^{-1}\,cm^{-1}}$. Both electrochemical and absorption spectroscopic data reveal that attachment of metal fragments close to the PBI core by an azabenzannulated PBI does not lead to a simple superposition of the separate ground state properties of the individual compounds (for example, PBI absorption), but creates hybrid states with new electronic features (for example, MLCT absorption at 520 nm in **1**).

The electrochemical and absorption spectroscopic results are rationalized by DFT and TD-DFT studies (BHandHLYP-D3BJ/def2-TZVP, gas phase; for details, see the Supporting Information), which suggest that the HOMO and HOMO−1 of **1** and **2** being PBI-based π-orbitals, while the metal d-orbitals are found to contribute to HOMO−2 to HOMO−4 and further low lying occupied MOs. The LUMO is in the case of the iridium complex **2** mainly located at the imide moieties of the PBI ligand, whereas in $[\mathrm{Ru(bpy)_2(ab\text{-}PBI)}][\mathrm{PF_6}]_2$ **1** the LUMO shows some additional contributions of one of the metal coordinating bipyridine ligands. The HOMO–LUMO gaps are found to be about 2.39 and 2.34 eV for **1** and **2**, respectively. The lowest energy band of **1** at 520 nm contains indeed some MLCT character, although it is mainly intraligand charge transfer (ILCT) in nature, and most of the higher-lying Franck-Condon (FC) singlet states are pure ILCT states (Figure 3a). In contrast, the S_1 state of **2** is a pure ILCT state, while the higher energy excitations observed in the range between 370–420 nm are of MLCT character. The experimental and theoretical findings show well a higher preference of $\mathrm{Ru^{II}}$ to undergo low-energy MLCT in comparison to $\mathrm{Ir^{III}}$. A similar analysis can also be applied to the FC triplet excited state T_1 (Figure 3b), which contains significant ^{3}MLCT contribution for **1** but is a pure ^{3}ILCT for **2**, giving rise to the experimental differences of these two types of excited states (see below), that is, a broad emission band for the ruthenium complex **1** and a well-resolved vibronic fine structure of the emission originating from the iridium compound **2**.

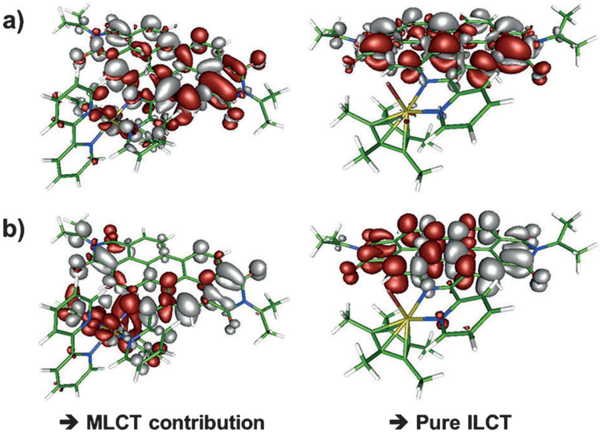

Figure 3. Calculated transition densities for a) FC-S_1 and b) FC-T_1 of **1** (left) and **2** (right), respectively, at the BHandHLYP-D3BJ/def2-TZVP level of theory.

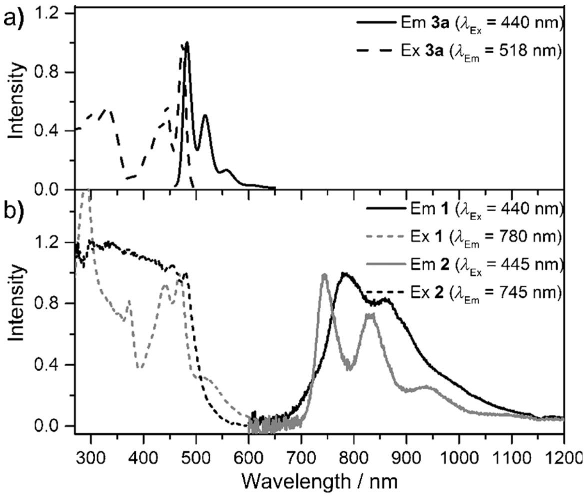

Figure 4. a) Emission (solid) and excitation spectra (dashed) of ab-PBI (only **3a** shown). b) Emission (solid) and excitation spectra (dashed) of **1** and **2**. All of the spectra were measured in degassed dichloromethane at 298 K.

The emission spectra of both complexes show an almost quantitative quenching of the ab-PBI fluorescence at 484 nm (Figure 4a; Supporting Information, Table S2). Instead, a long-lived emission in the NIR regime at 750–1000 nm appears with peak maxima at 780 nm for **1** and at 745 nm for **2** in degassed dichloromethane at room temperature (Figure 4b). Furthermore, the vibronic fine structures of the broad emission of **1** and the resolved band in **2** have energetic separations of about 1400 cm^{-1}, which is typical for PBI aromatic vibrations.[18] In line with our theoretical studies, we attribute the phosphorescence in **1** to originate from a mixed ^{3}ML(ab-PBI)/^{3}ILCT state, whereas emission in **2** is ^{3}IL(ab-PBI) in nature. The emission maxima of the complexes correspond to a ^{3}IL(PBI) energy of about 1.6 eV, which is significantly higher than the estimated value for bay-unsubstituted PBIs (1.2 eV).[19] A similar triplet excited-state energy of 1.68 eV has been found by Flamigni upon attachment of electron withdrawing functional groups at the perylene moiety.[7] Introduction of the electron-withdrawing aza-nitrogen in ab-PBI and the Lewis acidic metal fragments in **1** and **2** apparently stabilize the bonding PBI molecular orbitals to a greater extent than the anti-bonding MOs. As a consequence, a hypsochromic shift of the transitions originating from these frontier orbitals is observed in comparison to the parent PBI, which counts for the singlet excited states but even more for the triplet excited states (see triplet energies above). The accompanying smaller distance between the PBI S_1 and T_1 state and the presence of the intermediary MLCT state at 520 nm in **1** facilitate the T_1 population (for further details, see the Supporting Information, Figure S18).

The emission lifetime of the ruthenium **1** and iridium **2** complexes at room temperature in degassed dichloromethane were found to be 4.2 μs and 33 μs, respectively. Typical phosphorescence lifetimes of purely organic PBIs are around 100 μs[19] and thus the shorter lifetime of **1** indicates a strong spin–orbit coupling contribution of the metal center. Although iridium is the heavier 5d metal, this effect seems to be more pronounced for **1** than for **2**, which can be attributed to the higher degree of MLCT in the emissive state of the Ru complex (see above). Furthermore, $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ **1** displays a higher phosphorescence quantum yield ($\Phi_p = 11\,\%$) than **2** ($\Phi_p < 1\,\%$), and furthermore shows a more efficient phosphorescence than found for other ruthenium polypyridyl complexes,[20] exceeding even the 6% efficiency of $[Ru(bpy)_3]^{2+}$ itself (Supporting Information, Table S2).

In conclusion, we have reported the first example of a PBI-based transition-metal complex in which the metal fragment not only triggers the population of the triplet state in the PBI by ISC, but also shows a remarkable intense NIR phosphorescence with $\Phi_P = 11\,\%$ for $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ **1**. Photophysical and theoretical studies of the PBI-based Ru **1** and the Ir **2** complex underline the significance of metal orbital interactions with the PBI ligand for the spin-forbidden transitions $S_1 \rightarrow T_n$ and $T_1 \rightarrow S_0$. The fact that quantum yields in the NIR spectral region are intrinsically decreased due to the "energy-gap law" problem[21] makes the complex $[Ru(bpy)_2(ab\text{-}PBI)][PF_6]_2$ **1** with its high light absorptivity an interesting NIR-phosphorescence material.

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