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Long-Lived Room-Temperature Near-IR Phosphorescence of BODIPY in a Visible-Light-Harvesting N^C^N Pt^{II}–Acetylide Complex with a Directly Metalated BODIPY Chromophore**

Wanhua Wu, Jianzhang Zhao,* Huimin Guo, Jifu Sun, Shaomin Ji, and Zilong Wang^[a]

Abstract: Room-temperature longlived near-IR phosphorescence of boron-dipyrromethene (BODIPY) was observed $(\lambda_{\rm em} = 770 \text{ nm}, \Phi_{\rm P} = 3.5\%)$ $\tau_{\rm P} = 128.4 \,\mu {\rm s}$). Our molecular-design strategy is to attach Pt^{II} coordination centers directly onto the BODIPY π core using acetylide bonds, rather than on the periphery of the BODIPY core, thus maximizing the heavy-atom effect of Pt^{II}. In this case, the intersystem crossing (ISC) is facilitated and the radiative decay of the T₁ excited state of BODIPY is observed, that is, the phosphorescence of BODIPY. The complex shows strong absorption in the visible range ($\epsilon = 53800 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$ at 574 nm), which is rare for Pt^{II} -acetylide complexes. The complex is dual emissive with ³MLCT emission at 660 nm and the ³IL emission at 770 nm. The T₁ excited state of the complex is mainly localized on the BODIPY moiety (i.e. ³IL state, as determined by steady-state and time-resolved spectroscopy, 77 K emission spectra, and spin-density analysis). The strong visible-light-harvesting ability and long-lived T₁ excite state of the complex were used for triplet-trip-

Keywords: BODIPY • chromophores • phosphorescence • photochemistry • platinum let annihilation based upconversion and an upconversion quantum yield of 5.2% was observed. The overall upconversion capability ($\eta = \varepsilon \times \Phi_{UC}$) of this complex is remarkable considering its strong absorption. The model complex, without the BODIPY moiety, gives no upconversion under the same experimental conditions. Our work paves the way for access to transition-metal complexes that show strong absorption of visible light and long-lived ³IL excited states, which are important for applications in photovoltaics, photocatalysis, and upconversions, etc.

Introduction

Transition-metal complexes with populated triplet excited states upon excitation have attracted much attention, owing to their applications in electroluminescence.^[1-3] The representative compounds include Pt^{II} and Ir^{III} complexes, etc.^[1,4] Recently, these complexes have been found to have new applications in photocatalysis,^[5] optical limiting,^[6] molecular probes,^[7,8] and upconversions.^[9–14]

Concerning these new applications, the ability to have strong visible-light harvesting and to access the long-lived triplet-excited states are often very crucial. However, conventional N^N Pt^{II}-bis-acetylide complexes usually show weak absorption in the visible range and short T_1 excited-state lifetimes ($\tau < 5 \ \mu s$).^[1,4,15] Thus, it is important to develop new molecular design rationales for the preparation of

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[**] BODIPY=boron-dipyrromethene.

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transition-metal complexes that show intense absorption in the visible region and, at the same time, show long-lived T_1 excited states, to enhance the photophysical processes that these complexes are involved in. Concerning these demands, attaching a light-harvesting organic chromophore to the transition metal coordination center to prepare a dyad is one straight-forward strategy.^[14,16–20] However, the photophysics of these dyads are very often elusive; for example, the phosphorescence was quenched and short T_1 lifetimes were observed when perylenediimide (PDI) and boron-dipyrromethene (BODIPY) were used for the preparation of Pt^{II} and Ir^{III} complexes.^[21,22]

On the other hand, BODIPY is a particularly interesting chromophore,^[23,24] and has been incorporated into Pt^{II}, Ru^{II}, and Ir^{III} complexes to afford visible-light harvesting and long-lived T₁ excited states.^[18,22,25] However, the photophysical property of the components often collapse in the dyad. For example, for a BODIPY-containing Ru^{II} complex, the intrinsic metal-to-ligand charge-transfer (³MLCT) emission of the Ru^{II} coordination center was quenched and no long-lived triplet excited state was observed at room temperature (RT).^[18] Recently, a BODIPY-containing Ir^{III} complex was reported, in which again both the emission of the Ir^{III} coordination center and the fluorescence of the BODIPY moiety were quenched, the BODIPY-localized intraligand (³IL) state was populated (lifetime=25 µs, measured with time-resolved transient absorption difference spectrosco-

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py).^[22] Thus, in all of these reported BODIPY dyads, the RT phosphorescence of BODIPY was never observed and the T_1 excited-state lifetime was usually not very long.

After careful examination of the molecular structures of those pioneering BODIPY-containing dyads, we realized that the metal centers were attached onto the peripheral moieties of BODIPY, rather than to the π -conjugated BODIPY core. As a result, we envisaged that the heavy-atom effect of the transition metals in these dyads was not maximized, and thus the RT phosphorescence of BODIPY was never observed. Observation of RT phosphorescence usually requires a strong heavy-atom effect to facilitate the radiative ${}^{3}IL \rightarrow S_{0}$ intersystem crossing (ISC), that is, the phosphorescence.^[19]

To this end, herein we report the synthesis of complex Pt-1 (Scheme 1), in which two $N^{A}C^{N}$ Pt^{II}-coordinated units are connected to the π -core of BODIPY to maximize the heavy-atom effect of the Pt atom. Thus, we expected that the RT phosphorescence of BODIPY could be observed. We used the Pt^{II}-coordinated unit of complex Pt-2 for the construction of complex Pt-1.^[26] Complex Pt-2 was also used as a model complex in the study of the photophysical properties of these compounds. Complex Pt-1 shows strong absorption in the visible-light range and a long-lived T₁ excited state, as well as RT BODIPY phosphorescence. The population of the BODIPY-localized ³IL excited state for complex Pt-1 was confirmed by nanosecond time-resolved transient absorption difference spectroscopy, emission spectroscopy at 77 K, and DFT calculations (analysis of the spin-density surfaces and the molecular orbitals). The strong absorption of visible light and the long-lived T₁ excited state of complex

Pt-1 were ideal for sensitizing photophysical or photochemical processes; herein this sensitization is demonstrated by upconversion based on triplet–triplet annihilation (TTA).

Results and Discussion

Design and synthesis: To avoid non-radiative decay, the recently reported cyclometalated platinum(II) scaffold employed in the C^N^N complex of 2,6-bis(N-alkylbenzimidazol-2'-yl)benzene was used instead of the Pt^{II}-terpyridinecoordinated scaffold.^[1,26] The synthesis of complex Pt-1 uses the BODIPY chromophore as the starting material. After di-iodation at the 2- and 6-positions, two acetylide groups were attached to the BODIPY core (3) using Sonogashira coupling. Finally, a CuI-catalyzed reaction between the building block Pt-2 and BODIPY acetylide afforded the desired Pt-1 in good yield (64.9%; for more details, see the Experimental Section). It should be pointed out that the Pt^{II} centers are connected to the π -core of the BODIPY fluorophore. This unique structural profile has never been employed in the preparation of phosphorescent transitionmetal complexes with BODIPY.

Steady-state electronic spectroscopy (absorption and emission): The UV/Vis absorption spectra of compounds Pt-1, Pt-2, and the acetylide ligand BDP were studied (Figure 1). Compound Pt-2 showed a weak absorption in the visible range (absorption maxima centered at 414 nm, molar extinction coefficient $\varepsilon = 16200 \,\mathrm{m^{-1} \, cm^{-1}}$). However, for complex Pt-1, a strong absorption at 574 nm was observed ($\varepsilon =$



Scheme 1. Synthesis of complexes **Pt-1** and **Pt-2**, the structure of 2,6'-diiodo-bis-BODIPY (**4**; used as the standard for measuring the upconversion quantum yields), and the triplet-acceptor perylene (used in TTA upconversion). Reagents and conditions: i) H_3PO_4 , 230 °C, 4 h; ii) NaH, 1-bromobutane, DMF, 100 °C, overnight; iii) K_2PtCl_4 , HOAc, microwave; iv) dry CH_2Cl_2 , BF₃·OEt₂, NEt₃; v) NIS (4.0 equiv), RT; vi) trimethylsilylacetylene, [Pd-(PPh₃)₂Cl₂], PPh₃, CuI, NEt₃, reflux, 8 h; vii) Bu₄NF, THF, -78 °C; viii) CuI, CH₂Cl₂, (*i*Pr)₂NH.

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Figure 1. UV/Vis absorption spectra of complexes Pt-1, Pt-2, and acety-lide ligand **BDP** (toluene, 1.0×10^{-5} M; 20 °C).

53800 m⁻¹ cm⁻¹). This remarkably strong absorption in the visible range is very rare for Pt^{II}–acetylide complexes.^[1] The acetylide ligand **BDP** showed an absorption at 543 nm. Thus the significantly red-shifted absorption of complex **Pt-1** compared to the **BDP** ligand indicates a strong electronic interaction between the Pt^{II} center and the π -conjugated core of the BODIPY chromophore.^[21] Notably, the absorption of complex **Pt-1** in the visible region is more intense than most N^N Pt^{II}–bis-acetylide complexes.^[1,27,28]

Next, we studied the RT photoluminescence (Figure 2). Unlike complex **Pt-2**, which showed structured emission at 500–650 nm, highly red-shifted emission peaks at 660 nm



Figure 2. Normalized emission spectra of complexes **Pt-1** and **Pt-2**. **Pt-1**: MeOH, $\lambda_{ex} = 590$ nm; **Pt-2**: MeCN, $\lambda_{ex} = 420$ nm. 1.0×10^{-5} M. 20 °C.

and 770 nm were observed for complex **Pt-1**. Because the N^N Pt^{II} bis-acetylide complexes usually show emission peaks in the range 500–600 nm,^[1,27,28] we tentatively assigned the emission of complex **Pt-1** at 770 nm to the ³IL emission of the BOIDPY core (1.61 eV, see below). This assignment was supported by the T₁ energy level of the BODIPY acetylide ligand (**BDP**), which was calculated to be 821 nm (1.51 eV; see the Supporting Information). The RT phosphorescence quantum yield (Φ_P) of complex **Pt-1** was 3.5% (Table 1). To the best of our knowledge, this is the first time that the RT phosphorescence of BODIPY has been observed. None of the previously reported BODIPY-containing Pt^{II} and Ir^{III} complexes showed RT phosphorescence.^[18,22] One of those complexes showed phosphorescence of the BODIPY chromophore at 77 K (λ_{em} =

Table 1. Photophysical parameters of the Pt^{II} complexes and the BODIPY ligand.

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	$\lambda_{\rm abs}{}^{[a]}$	$\varepsilon^{[b]}$	Emission Properties		
			$\lambda_{em} [nm]^{[c]}$	$arPsi_{ m L}[\%]^{[{ m f}]}$	$ au^{[\mathrm{g}]}$
Pt-1	406/574	3.39/5.38	660/770 ^[d]	3.5 ^[e]	128.4 µs (RT)
					1.5 ms (77 K)
Pt-2	395/414	1.34/1.62	513/554	18.3	6.5 µs
BDP	543	8.58	560	54.4	6.0 ns

[a] In toluene $(1.0 \times 10^{-5} \text{ M})$. [b] Molar extinction coefficient. ε : $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. [c] In MeCN. [d] In MeOH. [e] In deaerated MeOH, with [Ru(phen)(bpy)₂](PF₆)₂ (ϕ =0.06 in MeCN) as a standard. [f] In MeCN, with BODIPY (ϕ =0.72 in THF) as a standard. [g] Luminescence lifetime at RT.

730 nm),^[22] which supports our assignment of the RT emission of complex **Pt-1** at 770 nm as the ³IL emission of the BODIPY ligand.

Interestingly, besides the emission band at 770 nm, an emission band was also observed at 660 nm for complex **Pt-1** (Figure 2). This emission was sensitive to O_2 and was significantly quenched in air, thereby indicating that it was a phosphorescence emission (Figure 2). Thus, we propose that the dual emissions of complex **Pt-1** at 660 nm and 770 nm are due to ³MLCT and the ³IL emissive state, respectively, and that the two triplet excited state are in equilibrium at RT.^[29] The energy difference between the two states is at least 2164 cm⁻¹ (0.27 eV, approximated as the distance between the two peaks).

To confirm that the dual emission of complex **Pt-1** at 660 nm/770 nm is due to the simultaneous emission from the equilibrated ³MLCT and ³IL states, rather than from one dual-emissive T₁ excited state, we measured the emission spectra of complex **Pt-1** at 77 K (Figure 3). Only the emission band at 775 nm was observed at 77 K. The thermally induced Stokes shift (ΔE_s) for this emission band was as small as 84 cm⁻¹, which is a clear indication of ³IL emission for this emission band at 770 nm.^[16b] We propose that, at 77 K, the ³MLCT state and the low-lying ³IL excited state are no longer in equilibrium because the upward transformation from the ³IL to the ³MLCT state is more difficult at 77 K than at RT; thus, only the emission from the ³IL state was observed.^[29]



Figure 3. Emission spectra of complex **Pt-1** in EtOH/MeOH (4:1 v/v) glass was at 77 K and solution at RT. $\lambda_{ex} = 590$ nm. The asterisk indicates a spike owing to the spectrometer.

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Nanosecond time-resolved transient difference absorption spectroscopy: Next, nanosecond time-resolved transient dif-

ference absorption spectra were studied (Figure 4). Upon



Figure 4. a) Time-resolved transient difference absorption spectra of complex **Pt-1** in deaerated MeOH (λ_{ex} =532 nm), and b) a decay trace of complex **Pt-1** at 550 nm, 25 °C.

pulsed-laser excitation, intense bleaching was found at 550 nm for complex **Pt-1**, which was due to depletion of the ground state of the **BDP** ligand. DFT calculations on the transient absorption spectra supported the assignment of the ³IL state for complex **Pt-1** (see the Supporting Information). The lifetime (τ) of the T₁ state of complex **Pt-1** was 125.8 µs (RT), which was consistent with the lifetime determined by luminescence (128.4 µs). This lifetime is the longest RT triplet excited-state lifetime ever reported for BODIPY. The previous values for BODIPY-localized ³IL states were 8–30 µs.^[18,22,25,30]

DFT calculations for assignment of the T₁ excited state: To confirm the ³IL nature of the T₁ state of complex **Pt-1**, the spin-density surfaces of complexes **Pt-1** and **Pt-2** were analyzed (Figure 5).^[19] For complex **Pt-2**, the spin density was distributed on the Pt^{II} center and on the N^C^N ligand; thus, the T₁ state of complex **Pt-2** could be safely assigned as a ³MLCT. However, the spin density for complex **Pt-1** was located on the BODIPY chromophore, whilst the N^C^N ligand and the Pt^{II} center made very small contributions. Thus, the lowest lying triplet state of complex **Pt-1** is the ³IL state.^[13,14,19] This theoretical prediction is consistent with the experimental results for the near-IR BODPY phosphorescence and with the long-lived triplet excited state of



Figure 5. Spin-density surfaces of complexes **Pt-1** and **Pt-2** at the optimized triplet-state geometry. Calculated at the DFT/B3LYP/6-31G(d)/ LANL2DZ level with Gaussian 09W.

complex **Pt-1**. Typically, the ${}^{3}IL$ state has a longer lifetime than the ${}^{3}MLCT$ state. ${}^{[31-33]}$

To assign the T_1 state of complex **Pt-1** from the perspective of molecular orbitals, the UV/Vis absorption and the phosphorescence of the complexes were studied by time-dependent DFT (TDDFT) analysis. The calculated absorption bands of complex **Pt-1** were at 570 nm and 429 nm (Table 2); these values were in good agreement with the ex-

Table 2. Electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI coefficients of the low-lying electronically excited states of complex **Pt-1**.^[a]

Electronic	TDDFT//B3LYP/6-31G(d)				
transition	Energy $[eVnm^{-1}]^{[b]}$	f ^[c]	Composition	CI ^[d]	Character
$S_0 \rightarrow S_1$	2.09/592	0.0003	$H-1 \rightarrow L+1$	0.1605	LLCT
			$H \rightarrow L + 1$	0.1343	LLCT
			$H \rightarrow L + 2$	0.6681	LLCT
$S_0 \rightarrow S_3$	2.17/570	0.6361	$H{-}4{\rightarrow}L$	0.1230	LLCT
			$H{-}2{\rightarrow}L$	0.1191	ILCT,MLCT
			$H \rightarrow L$	0.6769	ILCT,MLCT
$S_0 \rightarrow S_{10}$	2.89/429	0.4982	$H-4 \rightarrow L+1$	0.3293	LLCT
			$H-3\rightarrow L+2$	0.4689	LLCT
			$H-2 \rightarrow L+1$	0.3857	LLCT
$S_0 \rightarrow T_1^{[e]}$	1.39/892	$0.0000^{[f]}$	$H{-}6{\rightarrow}L$	0.1910	ILCT
			$H \rightarrow L$	0.6814	ILCT,MLCT
$S_0 \rightarrow T_2^{[e]}$	2.01/617	$0.0000^{[f]}$	$H{-}3{\rightarrow}L$	0.1229	LLCT
			$H{-}1{\rightarrow}L$	0.6771	ILCT,MLCT

[a] calculated at the TDDFT//B3LYP/6-31G(d)/LanL2DZ level. [b] Only selected low-lying excited states are presented. [c] Oscillator strength. [d] The CI coefficients are absolute values. [e] Based on optimized excited-state geometries. [f] No spin-orbit coupling was considered, thus f=0.

perimental values (Table 1 and Figure 1). The main components of the 570 nm absorption band were due to the HOMO \rightarrow LUMO transition, which was localized on the BODIPY units (Figure 6 and Table 2).



Figure 6. Frontier molecular orbitals for complex **Pt-1**, at the optimized S_0 state geometry. Calculated by DFT at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 09W.

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The triplet excited states were also studied by TDDFT calculations (Table 2). The calculated T_1 and T_2 states gave energy levels that were close to the experimental results (Figure 2 and Table 1). The molecular orbitals involved in the T_1 and T_2 states were mainly localized on the BODIPY ligand. These results were in agreement with the time-resolved transient absorption difference spectra and the spindensity analysis of the complex (Figure 4 and Figure 5).

The electronic spectra of the model complex, **Pt-2**, were also studied with the TDDFT methods (Table 3 and Figure 7). The calculated absorption maximum was located at 423 nm, which is close to the experimentally observed

Table 3. Electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI coefficients of the low-lying electronically excited states of complex **Pt-2**.^[a]

Electronic	TDDFT//B3LYP/6-31G(d)				
transition	Energy	$f^{[c]}$	Composition	$CI^{[d]}$	Character
	$[eV nm^{-1}]^{[b]}$	-	-		
$S_0 \rightarrow S_1$	2.93/423	0.1109	$H \! \rightarrow \! L$	0.7005	MLCT
$S_0 \rightarrow S_9$	3.74/332	0.2185	$H{-}4{\rightarrow}L$	0.1230	LLCT/ILCT
$S_0 {\rightarrow} T_1{}^{[e]}$	2.43/510	$0.0000^{[f]}$	$H{-}5{\rightarrow}L$	0.1476	ILCT
			$H-4 \rightarrow L+1$	0.1658	LLCT
			$H{-}2{\rightarrow}L$	0.4624	MLCT/ILCT
			$H{-}1{\rightarrow}L$	0.4317	LLCT
			$H \rightarrow L+1$	0.1233	MLCT

[a] Calculated at TDDFT//B3LYP/6-31G(d)/LanL2DZ level [b] Only selected low-lying excited states are presented. [c] Oscillator strength. [d] The CI coefficients are absolute values. [e] Based on the optimized excited state geometries. [f] No spin-orbit coupling was considered, thus f=0.



Figure 7. Frontier molecular orbitals for complex **Pt-2**, at the optimized S_0 state geometry. Calculated by DFT at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 09W.

value (414 nm; Figure 1 and Table 1). Furthermore, the oscillator strength for the $S_0 \rightarrow S_1$ transition was much smaller than that of the corresponding transition in complex **Pt-1** (Table 2); this trend is in agreement with the stronger absorption of complex **Pt-1**, compared to the UV/Vis absorption of complex **Pt-2** (Figure 1).

The T_1 energy level of complex **Pt-2** was calculated to be 510 nm, which was close to the experimentally observed phosphorescence of complex **Pt-2** (513 nm; Figure 2 and Table 1). The T_1 energy level of complex **Pt-2** (2.43 eV) was

remarkably different to that of the T_1 state energy level for the calculated complex **Pt-1** (1.39 eV); these results confirmed that the TDDFT method is reliable for the current complexes. Furthermore, the TDDFT calculation indicated that the frontier molecular orbitals of complex **Pt-2** are substantially different from those of complex **Pt-1**. For example, the $S_0 \rightarrow S_1$ transition of complex **Pt-2** can be recognized as a MLCT/IL transition (Figure 7), which is drastically different from that of complex **Pt-1**, for which an IL feature is prominent (Figure 6). Moreover, the T_1 excited state of complex **Pt-2** is mainly a 2,6-bis(*N*-alkylbenzimidazol-2'-yl)benzenelocalized ³IL state, which is entirely different from that of complex **Pt-1**, for which the T_1 state is localized on the BODIPY ligand (Figure 6 and Table 2).

Application in upconversion based on triplet-triplet annihilation: The intense visible-light absorption and the longlived triplet excited state of complex **Pt-1** are ideal for applications in sensitizing photophysical processes that need triplet excited states for initiation, such as upconversion based on triplet-triplet annihilation (TTA; see Scheme 2 for Ja-



Scheme 2. Jablonski diagram of triplet-triplet annihilation (TTA) upconversion, with complex **Pt-1** as the triplet sensitizer. TTET=triplet-triplet energy-transfer.

blonski diagram).^[9-12,34] Unlike other upconversion methods, such as two-photon absorption dyes or rare-earth materials,^[35-37] TTA upconversion is particularly interesting, owing to the low excitation power (a few mW cm⁻² is sufficient, the same scale as terrestrial solar-light intensity), the tunable excitation/emission wavelengths, and the high upconversion quantum yields. Triplet-triplet energy transfer (TTET) between the triplet sensitizer and the triplet acceptor/annihilator is the crucial process in TTA upconversion.

The current development of TTA upconversion faces some challenges; for example, triplet sensitizers are limited to Pt^{II}–porphyrin complexes to a large extent, for which the energy level of the T₁ state is difficult to change.^[9–11,34] Thus, new triplet sensitizers with intense visible-light absorptions, readily tunable T₁ state energy levels, and long-lived T₁ states were highly desired. Pt^{II}–acetylide complexes are ideal candidates because the aforementioned photophysical properties of these complexes can be readily tuned by changing the acetylide ligand, which is synthetically feasible.^[27,28,38]

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Recently, a N^N^N Pt^{II}–phenylacetylide complex was used as a triplet sensitizer for TTA upconversion.^[39] However, that complex showed weak absorption in the visible-light region ($\varepsilon = 7600 \,\mathrm{m^{-1} \, cm^{-1}}$ at 476 nm) and a short lifetime of the T₁ state ($\tau = 4.6 \,\mu$ s). As a result, the low upconversion quantum yield was observed ($\Phi_{\rm UC} < 1.1 \,\%$).^[39]

The Jablonski diagram of the TTA upconversion (Scheme 2) indicates that the visible-light-harvesting ability and the lifetime of the triplet excited state are two crucial properties for improving the efficiency of TTA upconversion. In principle, TTET is a bimolecular quenching process that follows the Stern–Volmer equation; thus the lifetime of the T_1 excited state of the triplet sensitizer is important: long-lived T_1 excited states will enhance the TTET process. Furthermore, strong absorption of the excitation light by the triplet sensitizer would produce more-concentrated sensitizers at the triplet excited state, thus the TTET process can also be enhanced. Therefore, the ideal triplet sensitizers for TTA upconversion would be those complexes that show strong absorption and long-lived T_1 excited states.

Because complex **Pt-1** shows precisely these desired photophysical properties, that is, intense absorption in visible region ($\varepsilon = 53800 \text{ m}^{-1} \text{ cm}^{-1}$ at 574 nm) and a long-lived T₁ excited state ($\tau_P = 128.4 \text{ µs}$, RT), it was used as a triplet sensitizer for TTA upconversion. Perylene was used as a triplet acceptor ($E_{T1}=1.53 \text{ eV}$, 810 nm). With excitation at 635 nm, complex **Pt-1** showed dual emission at 660 nm and 770 nm (Figure 8). In the presence of perylene, intense blue emis-



Figure 8. Upconversion with complex **Pt-1** as a triplet sensitizer $(1.0 \times 10^{-5} \text{ M})$. a) Emission spectra and b) photographs of the emission of sensitizers **Pt-1** and **Pt-2**, alone and in presence of perylene (Py; $4.0 \times 10^{-5} \text{ M}$). Excited with a red laser (λ_{ex} =635 nm, 20 mW), in deaerated MeOH, 20 °C.

sion in the range 400–550 nm was observed and both phosphorescence bands of complex **Pt-1** were completely quenched. Irradiation of perylene alone did not produce the blue emission, thereby verify the upconverted fluorescence. No upconversion was observed with complex **Pt-2** under the same conditions (see the Supporting Information). The upconversion with complex **Pt-1** as the triplet sensitizer was visible to the naked eye (Figure 8b).

The upconversion quantum yield with complex Pt-1 as the triplet sensitizer was 5.2%. Considering its intense absorp-

tion, the overall upconversion capability ($\eta = \varepsilon \times \Phi_{UC}$, where ε is the molar extinction coefficient of the triplet sensitizer and Φ_{UC} is the upconversion quantum yield) of complex **Pt-1** is significant. Previously, only the upconversion quantum yield (Φ_{UC}) was used to evaluate the upconversion capability of triplet sensitizers,^[9] but we propose that the η value is a more-reasonable parameter, especially where practical applications of the TTA upconversion are concerned, such as for photovoltaics.

Herein, we noticed two interesting results: 1) The dual emission bands of complex Pt-1 were both quenched with addition of perylene (Figure 8a); this observation indicates that both emission bands are due to triplet emissive excited states, which is in line with our previous conclusions. 2) The quenched phosphorescence peak area of complex Pt-1 is smaller than the peak area of the upconverted fluorescence band. This result goes against the traditional observations of TTA upconversion,^[9-11,32,34] where the generation of upconverted fluorescence is accompanied by significant quenching of the phosphorescence of the triplet sensitizer. Our observation implies that triplet sensitizers at the T₁ excited states that are otherwise non-emissive were involved in the TTET process. Thus, we suggest that weakly phosphorescent, or even non-phosphorescent, transition-metal complexes can be used as triplet sensitizers for TTA upconversion.^[12b,20] At present, most of the utilized triplet sensitizers are phosphorescent.^[9,11] In fact, the phosphorescence of these triplet sensitizers are detrimental to the TTA upconversion because the radiative decay of the T_1 excited state of sensitizer (i.e. the phosphorescence) is in competition with TTET (Scheme 2).

Quenching of the dual phosphorescence of complex **Pt-1** with perylene was studied quantitatively (Figure 9). The emission at 770 nm was quenched more-significantly than that at 660 nm. In this case, Föster quenching of the emission of complex **Pt-1** by perylene is impossible, owing to the unmatched singlet excited state energy levels and the distance between complex **Pt-1** and perylene molecules in solution. Thus, the Dexter mechanism is responsible for the phosphorescence quenching of complex **Pt-1**, that is, by TTET from complex **Pt-1** to perylene. The Stern–Volmer



Figure 9. a) Quenching of the phosphorescence of complex **Pt-1** by perylene; b) Stern–Volmer plots of complexes **Pt-1** and **Pt-2** with perylene (for **Pt-1**) or 9,10-diphenylanthracene (DPA, for **Pt-2**) as triplet acceptors (quencher). c[**Pt-1**]or c[**Pt-2**]= 1.0×10^{-5} M. λ_{ex} =590 nm for **Pt-1** and 430 nm for **Pt-2**. In deaerated MeOH, 20 °C.

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fitting showed a downward curvature (Figure 9), which clearly indicated that two excited species with different lifetimes were responsible for the quenching (Table 4). For complex **Pt-2**, only one quenching constant was observed

Table 4. Upconversion-related parameters of the Pt^{II} complexes.^[a]

	$K_{\rm sv} [imes 10^{-3} { m m}^{-1}]^{[{ m b}]}$	$arPhi_{ m UC}[\%]^{[c]}$
Pt-1	$K_{\rm sv}^{1} = 3.6 \ (13.3)^{[d]}$	5.2
Pt-2	$K_{\rm sv}^2 = 1232.2 \ (80.7)^{\rm reg}$ 40.7	0.0

[a] In deaerated CH₃OH (1.0×10^{-5} M; 20 °C). [b] Stern–Volmer quenching constant. [c] Upconversion quantum yields. [d] The two quenching constants (the numbers in the parenthesis are the percentage ratios of the components).

(Figure 9b). It should be pointed out that 9,10-diphenylanthracene (DPA) was used as triplet acceptor for the quenching studies of complex **Pt-2** rather than perylene. This change was because the excitation wavelength of complex **Pt-2** is shorter than that of complex **Pt-1** (Figure 1), and so perylene can be excited at the excitation wavelength of complex **Pt-2**.^[9b]

Conclusion

Room-temperature long-lived near-IR phosphorescence of BODIPY was observed ($\lambda_{em} = 770 \text{ nm}, \Phi_P = 3.5\%, \tau_P =$ 128.4 µs). Our unique molecular-design strategy is to attach Pt^{II} coordination centers directly onto the BODIPY π -core using acetylide bonds, thereby maximizing the heavy-atom effect of Pt^{II}. Intersystem crossing (ISC) is facilitated and the radiative decay of the T₁ excited state of BODIPY is observed, that is, the phosphorescence of BODIPY. The complex shows intense absorption in visible range ($\varepsilon =$ $53800 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$ at 574 nm). The complex is dual emissive at 660 nm and 770 nm. The T_1 excited state of the complex is mainly localized on the BODIPY moiety (i.e. ³IL state, as determined by steady-state and time-resolved spectroscopy, 77 K emission spectra, and spin-density analysis). The intense visible-light-harvesting ability and long-lived T₁ excite state of the complex were used for triplet-triplet annihilation upconversion and an upconversion quantum yield of 5.2% was observed. Our work paves the way for access to transition-metal complexes that show strong absorption of visible light and long-lived ³IL excited states, which are important for applications in photovoltaics, photocatalysis, and upconversions.

Experimental Section

All of the chemicals used were analytical pure and used as received. Solvents were dried and distilled before use. UV/Vis absorption spectra were measured with an Agilent 8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Shimadzu 5301 PC spectrofluorometer or on a Sanco 970 CRT spectrofluorometer. Fluorescence/phosphorescence lifetimes were measured on a Horiba Jobin Yvon Fluoro Max-4

(TCSPC) instrument. The nanosecond time-resolved transient absorption difference spectra were measured by Edinburgh analytical instruments (LP 920, Edinburgh Instruments, Livingston, U.K.) and recorded on a Tektronix TDS 3012B oscilloscope. All samples in flash photolysis experiments were deaerated with argon for approximately 15 min before measurement and the gas flow was kept constant during the measurement. Luminescence quantum yield of complex Pt-1 was measured with [Ru- $(bpy)_2(Phen)](PF_6)_2$ ($\Phi = 6.0\%$ in deaerated CH₃CN) as the reference and the other values were measured with BODIPY as the reference ($\Phi =$ 0.72 in THF). The luminescent photographs were obtained using a Samsung NV 5 digital camera. The exposure time was the default value of the camera. A diode-pumped solid-state (DPSS) laser was used for the upconversions. The samples were purged with N2 or Ar for 15 min before measurement. The upconversion quantum yields were determined with 2,6'-diiodo-BODIPY ($\Phi = 9.3\%$ in toluene; see Scheme 1 for the molecular structure) as the standard.

The density functional theory (DFT) calculations were used for optimization of the ground-state and excited-states geometries. The energy level of the singlet and triplet states of the acetylide ligand (**BDP**) and the complexes were calculated with by time-dependent DFT (TDDFT) analysis. The spin-density surfaces of complexes **Pt-1** and **Pt-2** were calculated with the optimized triplet-state geometries.

1,3,5,7-Tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (3): Under a nitrogen atmosphere, benzoyl chloride (2.8 g, 0.021 mol) and 2,4-dimethylpyrrole (4 mL, 3.7 g, 0.04 mol) were added to dry CH₂Cl₂ (150 mL) using a syringe. The mixture was stirred at RT overnight, then Et₃N (20 mL) and BF₃·Et₂O (20 mL) were added under ice-cold conditions, and the reaction mixture was stirred for 1 h. Next, the mixture was poured into water (200 mL), and the organic layer was collected, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/*n*-hexane, 1:1 v/v) to give compound **3** as a red powder (2.3 g, yield: 33.3 %). ¹H NMR (400 MHz, CDCl₃): δ =7.49–7.47 (m, 3H), 7.29–7.26 (m, 2H), 5.98 (s, 2H), 2.56 (s, 6H), 1.37 ppm (s, 6H).

2,6-Diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene

(4):^[14b] To a solution of compound **3** (200 mg, 0.62 mmol) in dry CH₂Cl₂ (25 mL) was added excess *N*-iodosuccinimide (NIS; 558 mg, 2.48 mmol). The mixture was stirred at RT for about 30 min (monitored by TLC until the starting material had been completely consumed). The reaction mixture was then concentrated under vacuum, and the crude product was purified by column chromatography on silica gel (*n*-hexane/CH₂Cl₂, 2.1 v/ v). The red band was collected and the solvent was removed under reduced pressure to obtain a red solid (300.0 mg, yield: 84.0%). ¹H NMR (400 MHz, CDCl₃): δ =7.54–7.51 (m, 3H), 7.26–7.24 (m, 2H), 2.65 (s, 6H), 1.38 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ =156.91, 145.52, 141.52, 134.44, 129.69, 129.62, 127.91, 85.84, 17.12, 16.22 ppm; HRMS (MALDI): *m*/z calcd for [C₁₉H₁₇BF₂I₂N₂]⁻ 575.9542; found: *m*/z: 575.9528.

 $2, 6-Diethynyl {-} 1, 3, 5, 7-tetramethyl {-} 8-phenyl {-} 4, 4-difluoroboradia zainda cene$ (BDP): Under an argon atmosphere, compound 4 (280.0 mg, 0.49 mmol), [Pd(PPh₃)₂Cl₂] (34.0 mg, 0.049 mmol), PPh₃ (26.8 mg, 0.10 mmol), and CuI (19.4 mg, 0.10 mmol) were mixed in (iPr)₂NH (5 mL) and THF (10 mL). After stirring, trimethylsilylacetylene (190.6 mg, 1.94 mmol) was added using a syringe. The solution was stirred at 60°C for 4 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (CH2Cl2) to obtain a darkred solid. Bu₄NF·3H₂O (1 m in THF, 1.2 mL) was added dropwise to a solution of the above trimethylsilyl-protected intermediate (150 mg, 0.29 mmol) in 5 mL THF at -78 °C and the solution was kept at -78 °C for about 1 h. Next, CH₂Cl₂ (100 mL) and water (50 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3×15 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous MgSO4, and the solvent was removed under reduced pressure. The residue was purified by passing through a silica plug (CH₂Cl₂) to give a red solid (80 mg, 0.21 mmol, yield: 73.6 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.53-7.52$ (m, 3 H), 7.26-7.24 (m, 2H), 3.31 (s, 2H), 2.65 (s, 6H), 1.46 ppm (s, 6H). ¹³C NMR A EUROPEAN JOURNAL

(100 MHz, CDCl₃): δ =159.00, 145.70, 143.30, 134.40, 131.10, 129.64, 129.56, 127.86, 115.32, 84.30, 76.07, 13.68, 13.40 ppm. HRMS (EI): *m/z* calcd for [C₂₃H₁₉N₂F₂B]⁺ 372.1609; found: 372.1612.

Complex Pt-1: Under an argon atmosphere, complex Pt-2 (48.0 mg, 0.074 mmol) and BDP (13.2 mg, 0.037 mmol) were dissolved in a mixed solvent system of diisopropylamine (1.0 mL) and CH₂Cl₂ (5 mL). The mixture was deaerated with argon, then CuI (5 mg, 0.09 mmol) was added and the mixture was stirred at RT overnight. The mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel (CH2Cl2/CH3OH, 100:1, v/v). The purple band was collected, and 38.0 mg of purple powder was obtained, yield: 64.9%. ¹H NMR (400 MHz, CDCl₃/[D₆]DMSO): $\delta = 8.39$ (d, 2H, J = 8.0 Hz), 7.94-7.92 (m, 3H), 7.68-7.62 (m, 9H), 7.45-7.37 (m, 7H), 7.19-7.17 (m, 1H), 7.12–7.08 (m, 3H), 6.94 (t, 1H, J=7.8 Hz), 6.60 (t, 1H, J=8.4 Hz), 4.67-4.29 (m, 8H), 2.91 (s, 6H) 2.02-1.79 (m, 8H), 1.76 (s, 6H), 1.53-1.40 (m, 8H), 1.02–0.85 ppm (m, 12H); 13 C NMR (100 MHz, CDCl₃+ $[D_6]DMSO$): $\delta = 160.96$, 156.13, 143.20, 132.40, 132.22, 131.87, 123.94, 122.83, 122.47, 122.30, 116.41, 116.25, 112.88, 109.86, 108.83, 89.60, 76.15, 45.94, 43.77, 31.18, 28.66, 19.05, 12.96 ppm. HRMS (MALDI): m/z calcd for [C₇₉H₇₅N₁₀Pt₂BF₂]⁺ 1602.5533; found: *m*/*z* 1602.5460.

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