# Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

# Ping-Pong Energy Transfer in a Boron Dipyrromethane Containing Pt(II)-Schiff Base Complex: Synthesis, Photophysical Studies, and Anti-Stokes Shift Increase in Triplet–Triplet Annihilation **Upconversion**

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# Supporting Information

**ABSTRACT:** A boron dipyrromethane (BDP)-containing Pt(II)-Schiff base complex (Pt-BDP), showing ping-pong singlet-triplet energy transfer, was synthesized, and the detailed photophysical properties were investigated using various steady-state and time-resolved transient spectroscopies. Femtosecond/nanosecond transient absorption spectroscopies demonstrated that, upon selective excitation of the BDP unit in Pt-BDP at 490 nm, Förster resonance energy transfer from the BDP unit to the Pt(II) coordination center occurred (6.7 ps), accompanied by an ultrafast intersystem crossing at the Pt(II) coordination center (<1 ps) and triplet-triplet energy transfer back to the BDP moiety (148 ps). These processes generated a



triplet state localized at BDP, and the lifetime was 103.2 µs, much longer than the triplet-state lifetime of Pt-Ph (3.5 µs), a complex without the BDP moiety. Finally, Pt-BDP was used as a triplet photosensitizer for triplet-triplet annihilation (TTA) upconversion through selective excitation of the BDP unit or the Pt(II) coordination center at lower excitation energy. An upconversion quantum yield of up to 10% was observed with selective excitation of the BDP moiety, and a large anti-Stokes shift of 0.65 eV was observed upon excitation of the lower-energy band of the Pt(II) coordination center. We propose that using triplet photosensitizers with the ping-pong energy-transfer process may become a useful method for increasing the anti-Stokes shift of TTA upconversion.

# INTRODUCTION

Transition-metal complexes have attracted much attention in recent years because of their potential applications in photocatalysis,<sup>1</sup> photovoltaics,<sup>2,3</sup> electroluminescence,<sup>4,5</sup> luminescence bioimaging and molecular sensing,  $^{6-13}$  photodynamics,  $^{14-16}$  fundamental photochemistry studies,  $^{17-22}$  and, more recently, triplet-triplet annihilation (TTA) upconversion.<sup>23-28</sup> Although many transition-metal complexes have been proposed as triplet photosensitizers for TTA upconversion, developing efficient triplet photosensitizers is still challenging. One example is Pt(II) complexes,<sup>29-32</sup> which are promising candidates because of their efficient intersystem crossing (ISC) and strong absorption of visible light.<sup>26,27</sup> Furthermore, their feasible preparation and derivatization, chemical stability, and photostability make Pt(II) complexes suitable for TTA upconversion.

One of the remaining problems in TTA upconversion is the small anti-Stokes shift, i.e., the energy difference between

excitation and the upconverted emission wavelength (note that the application of the term anti-Stokes shifts is different from the original meaning of Stokes shift, which means that the same electronic states are involved for the excitation and emission). $^{33-36}$  Castellano and co-workers used a Ru(II)/ Zn(II) trinuclear complex for TTA upconversion, and the anti-Stokes shift is up to 0.71 eV.<sup>37</sup> Normally, TTA upconversion with transition-metal complexes as triplet photosensitizers is with anti-Stokes shifts smaller than 0.5 eV.38-42 Recently, one promising method was reported to increase the anti-Stokes shift by using photosensitizers with a relatively strong  $S_0 \rightarrow T_1$ absorption because such direct excitation to the T1 state is possible, the energy loss of the  $S_1 \rightarrow T_1$  ISC process in normal aromatic triplet photosensitizers is avoided, and the anti-Stokes shift is up to 0.86 eV.<sup>43</sup> However, such complexes are limited,

Received: November 28, 2017

#### Scheme 1. Synthesis of the Complexes<sup>a</sup>



<sup>*a*</sup>The molecular structures of the ligands and reference complex **Pt-Ph** are also shown: (i) EtOH, acetic acid, reflux; (ii)  $K_2CO_3$ ,  $K_2PtCl_4$ , DMSO, 75 °C, 12 h; (iii) pinacol, toluene, 120 °C, 12 h; (iv) (a) 2,4-dimethylpyrrole, trifluoroacetic acid, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 12 h; (b) Et<sub>3</sub>N, BF<sub>3</sub>·OEt<sub>2</sub>, room temperature, 2 h; (v) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene/EtOH/water, Na<sub>2</sub>CO<sub>3</sub>; (vi) phenylboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene/EtOH/water, K<sub>2</sub>CO<sub>3</sub>.

and in most compounds, the  $S_0 \rightarrow T_1$  transition is strongly forbidden, which leads to a small oscillator strength and thus weak absorption. Furthermore, because of the strong heavyatom effect, which is crucial for the  $S_0 \rightarrow T_1$  transition, the triplet state is short-lived  $(T_1 \rightarrow S_0 \text{ ISC} \text{ is enhanced})$ . Although  $S_0 \rightarrow T_1$  absorptivity is important to improve the anti-Stokes shifts of TTA upconversion, the  $S_0 \rightarrow T_1$  absorptivity is weak, which is detrimental to the efficiency of TTA upconversion. Moreover, the triplet-state lifetime of the Os(II) coordination center is short; thus, much room is left for using Os(II) complexes as triplet photosensitizers to attain efficient TTA upconversion with large anti-Stokes shifts and efficient TTA upconversion. Another strategy to increase the anti-Stokes shift of TTA upconversion is to use photosensitizers with a small  $S_1/$ T<sub>1</sub> energy gap and thus a high-T<sub>1</sub> triplet-state energy level. However, for most  $\pi$ -conjugated organic chromophores, such as boron dipyrromethane (BDP) dyes,<sup>44</sup> the  $S_1/T_1$  energy gap is large because of the strong electron-exchange effects [] values, which are proportional to the spatial overlap of the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO); the  $S_1/T_1$  state energy gap is 2J]. Thus, the energy loss, via the  $S_1 \rightarrow T_1$  ISC of the photosensitizer, is unavoidable for TTA upconversion.

Herein, we prepared a Pt(II)—Schiff base complex containing a visible-light-harvesting BDP appendent (complex **Pt-BDP**; Scheme 1). The complex shows broad-band absorption in the visible spectral region, and it is used for TTA upconversion to attain a large anti-Stokes shift. Our method it to attach a spinconverter moiety to the BDP moiety, thus "inserting" singlet and triplet energy levels between the S<sub>1</sub> and T<sub>1</sub> state energy levels of BDP. The Pt(II) coordination framework attached to BDP serves as a singlet energy acceptor and spin converter to collect the S<sub>1</sub> state energy of BDP via intramolecular Förster resonance energy transfer (FRET) and convert the singlet spin state to the triplet state with the heavy-atom effect of Pt(II). Note that the Pt(II) coordination framework is with a lower S<sub>1</sub> state energy level but a higher  $T_1$  state energy level than the BDP appendant. Finally, the energy is transferred to the  $T_1$  state of the BDP unit through intramolecular triplet-triplet energy transfer (TTET). Ping-pong energy transfer (singlet-triplet energy transfer) is a known concept, and several examples have been reported, but it was rarely used for TTA upconversion.<sup>45-55</sup>

To achieve the aim of being a spin converter, the coordination center moiety should satisfy the following conditions: it should be with a lower S1 state energy level but a  $T_1$  state energy level higher than BDP and, most importantly, an efficient ISC. Pt(II)-Schiff base complexes can be good candidates for the spin-converter moiety because they satisfy all conditions listed above. Although the Pt(II)-Schiff base complexes are potent spin converters, studies on the photophysical properties of this type of phosphorescent Pt(II)-Schiff base complex are rare.<sup>24</sup> Previously, Che et al. reported a series of Pt(II)-Schiff base complexes and the photoluminescence, triplet excited state, and electroluminescence properties were studied.<sup>56</sup> Borisov et al. prepared red-light-absorbing Pt(II)-Schiff base complexes, the application for TTA upconversion was studied, and the anti-Stokes shift was 0.36 eV.57 These complexes contained a single chromophore; thus, there was only one major absorption band in the visible range. Previously, we prepared Pt(II)-Schiff base complexes attached with pyrenyl moieties, in which intramolecular triplet energy transfer was observed and the T1 state was the pyrenyl moiety-localized  ${}^{3}$ IL state (IL = intraligand), not the conventional  ${}^{3}$ MLCT state (MLCT = metal-to-ligand charge transfer).<sup>58</sup>

In this study, we prepared an exemplar Pt(II)-Schiff base complex containing a BDP chromophore on the coordination framework (**Pt-BDP**; Scheme 1). With femtosecond/nanosecond transient absorption (fs/ns-TA) spectroscopy, we elucidated the kinetics of the forward singlet energy transfer and backward triplet energy transfer to the BDP chromophore and the ISC process. We examined the complex as a triplet photosensitizer for TTA upconversion. Indeed, through the ping-pong energy-transfer pathway, we obtained upconversion quantum yields of up to 10% with the excitation of BDP. Furthermore, a large anti-Stokes shift of 5290 cm<sup>-1</sup> (0.65 eV) was observed, compared to the direct excitation of the BDP moiety (anti-Stokes shift of 2660 cm<sup>-1</sup>, 0.33 eV) upon excitation of the lowest absorption band of the Pt(II)–Schiff base complex.

# RESULTS AND DISCUSSION

Molecular Design and Synthesis. Previously, Pt(II)-Schiff base complexes containing no linked chromophores were reported and examined as triplet sensitizers for TTA upconversion.<sup>57</sup> Recently, we prepared a pyrenyl-containing Pt(II)-Schiff base complex and observed the triplet-state equilibrium and population of the <sup>3</sup>IL state.<sup>58</sup> To improve the light-harvesting efficiency of chromophores and attain efficient triplet-state localization on the linked chromophore rather than the Pt-Schiff base complex-localized <sup>3</sup>MLCT state thus to extend the triplet-state lifetime, we synthesized a new system combining a Pt(II)-Schiff base coordination center and a BDP appendant (Pt-BDP; Scheme 1). The BDP chromophore was selected as an appendant because of its feasible derivatization, high photostability, strong absorption of visible light, and, most importantly, lower triplet-state energy and longer triplet-state lifetime than those of the Pt(II)–Schiff base complex.<sup>59–65</sup> Pt(II),<sup>66–69</sup> Ir(III),<sup>70–72</sup> Ru(II),<sup>73–75</sup> and Re(I) complexes<sup>76</sup> containing BDP ligands have been reported, but this is the first time that a Pt(II)-Schiff base complex linked with BDP has been reported.

The synthesis of **Pt-BDP** is outlined in Scheme 1. The ligand 1 was synthesized from 3,5-di-*tert*-butylsalicylaldehyde and 4bromo-1,2-diaminobenzene under reflux conditions. Then the metalation of the Schiff base with  $K_2PtCl_4$  gives the intermediate Pt(II) complex 2. The Suzuki coupling reaction of complex 2 with phenylboronic acid gave the reference complex **Pt-Ph**. The Suzuki coupling reaction of BDP 4 with 2 gave the target Pt(II) complex (**Pt-BDP**) in 38% yield. All compounds were well characterized using <sup>1</sup>H NMR and high-resolution mass spectrometry (HRMS). Single-crystal X-ray analysis was carried out for **Pt-Ph**.

**Single-Crystal Molecular Structure.** The molecular structure of **Pt-Ph** was determined by single-crystal X-ray diffraction (Figure 1 and Table S1). For **Pt-Ph**, the Pt(II) coordination centers formed an orthorhombic crystal system with square-planar geometries. Bond lengths and angles were consistent with those reported for typical Pt(II)–Schiff base



**Figure 1.** Perspective view of the single-crystal molecular structure of **Pt-Ph** with 50% thermal ellipsoid (H atoms are omitted for clarity).

complexes.<sup>56</sup> The bond angles among N1–Pt1–N2, N1–Pt1–O1, N2–Pt1–O2, N2–Pt1–O1, N1–Pt1–O2, and O1–Pt1–O2 were 83.9(3)°, 94.7(3)°, 95.6(3)°, 176.8(3)°, 176.7(3)°, and 86.0(2)°, respectively. The bond lengths of Pt1–O1, Pt1–O2, Pt1–N1, and Pt1–N2 were 1.964, 1.973, 1.940, and 1.921 Å, respectively, which were close to the previously reported values (1.921–2.015 Å).<sup>4</sup> The C–N, C–O, and C–C bond lengths were in the range of 1.193–1.470 Å, which are close to the literature values (1.192–1.233 Å).<sup>57</sup> The **Pt-Ph** packing structure shows an arrangement of molecules at the corners, which is specific to orthorhombic systems in the dorsal and front views, and the presence of bulky *tert*-butyl groups effectively inhibits intermolecular  $\pi$ – $\pi$ -stacking interactions of the aryl rings.

Steady-State UV-Vis Absorption and Emission Spectra. The UV-vis absorption of Pt-BDP and the reference compounds Pt-Ph and BDP was studied (Figure 2). The



**Figure 2.** (a) UV–vis absorption spectra of **Pt-BDP**, **Pt-Ph**, and BDP. (b) Photoluminescence spectra of **Pt-BDP** under air and N<sub>2</sub> atmospheres.  $\lambda_{ex} = 475$  nm.  $c = 1.0 \times 10^{-5}$  M in toluene, 20 °C.

complex **Pt-Ph** shows a low-energy band at 575 nm ( $\varepsilon = 6.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), which can be assigned to the  $S_0 \rightarrow {}^{1}\text{MLCT}/{}^{1}\text{IL}$  transitions of the Pt(II) coordination center, while the higherenergy bands at 486 nm ( $\varepsilon = 5.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 393 nm ( $\varepsilon = 2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) can be assigned to the  $\pi - \pi^*$  transition of the coordinated Schiff base ligand.<sup>56</sup> **Pt-BDP** shows one major absorption band at 578 nm ( $\varepsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), due to the  $S_0 \rightarrow {}^{1}\text{MLCT}/{}^{1}\text{IL}$  transition, and a second strong absorption band at 504 nm ( $\varepsilon = 7.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), which originates from the BDP chromophore. The same strong band is observed in the BDP absorption spectrum.

The absorption spectrum of **Pt-BDP** resembles the sum of the **Pt-Ph** and BDP spectra, and the peaks from neither the Pt– Schiff base complex nor the linked BDP unit are shifted. These features suggest that there are no significant electronic interactions between the Pt(II) coordination center and the BDP chromophore at the ground state.<sup>45–47</sup>

Under aerated conditions, **Pt-BDP** shows a single emission band at 515 nm, which can be assigned to the residual fluorescence of the BDP unit (Figure 2b). Under a  $N_2$ atmosphere, an additional red-shifted emission band at 652 nm was observed, which can be assigned to phosphorescence from the Pt(II) coordination center. This assignment is supported by the phosphorescence of **Pt-Ph** observed at 650 nm (Table 1). Similar results were observed in other solvents such as dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), acetonitrile (CH<sub>3</sub>CN), and methanol (MeOH) (Figure S13). We found that **Pt-BDP** is unstable upon photoirradiation; the resulting slight decomposition may induce a stronger emission at 515 nm.

To investigate the characteristics of the emissive states in **Pt-BDP** and **Pt-Ph**, the emission spectra at 77 K are also studied

	$\lambda_{abs}^{a}/nm$	$\varepsilon^{b}$	$\lambda_{\rm em}^{a}/{\rm nm}$	$\Phi_{ m L}/\%$	$\Phi_{\Delta}{}^{e}/\%$	$\Phi_{\mathrm{T}}{}^{g}$ / %	$ au_{ m L}/ m ns$	$ au_{\mathrm{T}}^{j}/\mu\mathrm{s}$
Pt-BDP	396	4.5	515/650	$0.20^{c}/0.28^{d}$	77 <sup>e</sup> /51 <sup>f</sup>	89	$\tau_{\rm F}$ = 0.085 ns (99%), 4.8 ns (1%) <sup>h</sup>	103.2
	504	7.8					$\tau_{\rm P}$ = 18.3 ns (98%) 3.9 $\mu$ s (2%) <sup>i</sup>	
	578	1.1						
Pt-Ph	393	2.4	650	$4.4^{c}/11^{d}$	$60^{e}/58^{f}$	40	$0.77 \text{ ns}^h$	3.5
	486	0.05					3.7 $\mu s^i$	
	575	0.06						
BDP	473	2.12	526	83 <sup>c</sup>			3.8 ns	
	503	10.5						

|--|

<sup>*a*</sup>In toluene ( $1.0 \times 10^{-5}$  M), 20 °C. <sup>*b*</sup>Molar extinction coefficient at the absorption maxima.  $\varepsilon = 10^4$  M<sup>-1</sup> cm<sup>-1</sup>. <sup>*c*</sup>Fluorescence quantum yields. DiiodoBDP ( $\Phi_F = 2.7\%$  in CH<sub>3</sub>CN) was used as the standard. <sup>*d*</sup>Phosphorescence quantum yields. DiiodoBDP ( $\Phi_F = 2.7\%$  in CH<sub>3</sub>CN) was used as the standard. <sup>*d*</sup>Phosphorescence quantum yields. DiiodoBDP ( $\Phi_F = 2.7\%$  in CH<sub>3</sub>CN) was used as the standard. <sup>*e*</sup>The quantum yield of <sup>1</sup>O<sub>2</sub> with diiodoBDP ( $\Phi_{\Delta} = 70\%$  in CH<sub>3</sub>OH;  $\lambda_{ex} = 500$  nm) is used as the standard. <sup>*f*</sup>The quantum yield of <sup>1</sup>O<sub>2</sub> with styrylBDP (59% in toluene;  $\lambda_{ex} = 580$  nm) is used as the standard. <sup>*g*</sup>Triplet-state quantum yield, with diiodoBDP ( $\Phi_T = 87\%$  in CH<sub>2</sub>Cl<sub>2</sub>;  $\lambda_{ex} = 532$  nm) as the standard. <sup>*h*</sup>Fluorescence lifetimes. <sup>*i*</sup>Phosphorescence lifetimes. <sup>*j*</sup>Triplet-state lifetime determined with ns-TA spectroscopy.  $\lambda_{ex} = 532$  nm.  $c = 1.0 \times 10^{-5}$  M in degassed toluene. The estimated error is ca. ±5%.

(Figure 3). For both **Pt-BDP** and **Pt-Ph**, the emission band at 645 nm is blue-shifted by about 470  $\text{cm}^{-1}$  at 77 K compared to



Figure 3. Normalized emission spectra of (a) Pt-BDP and (b) Pt-Ph in degassed MeOH/EtOH (1:4, v/v) at room temperature and 77 K (frozen solution).  $\lambda_{ex} = 445$  nm.  $c = 1.0 \times 10^{-5}$  M.

the room temperature emission band (Figure 3). This large thermally induced increase in the emission energy observed in a rigid matrix indicates the MLCT feature of the emissive triplet state of the Pt(II)–Schiff base complex. The emissive triplet state of the pendant BDP chromophore in **Pt-BDP** is expected to be located in the lower-energy region (>730 nm).<sup>77</sup>

Compared to BDP and **Pt-Ph**, **Pt-BDP** shows significantly quenched fluorescence and phosphorescence emission (Figures 4 and S14). In **Pt-BDP**, because BDP and the Pt(II) coordination center do not show electronic interactions, the possible deactivation pathways of the emissive singlet and triplet states can be attributed to two major processes: FRET and photoinduced electron transfer (PET) from BDP to the



Figure 4. Comparison of the emission spectra of (a) **Pt-BDP** and **BDP** ( $\lambda_{ex} = 475 \text{ nm}$ ) and (b) **Pt-BDP** and **Pt-Ph** ( $\lambda_{ex} = 550 \text{ nm}$ ). Optically matched solutions were used.  $c = \text{ca.} 1.0 \times 10^{-5} \text{ M}$  in degassed toluene, 20 °C.

Pt(II) coordination center. By calculating the Gibbs free-energy changes of the putative PET process, we find that PET is prohibited in toluene (see the electrochemical study section); thus, we expect that fluorescence is quenched by the FRET process. Similarly, phosphorescence quenching of the Pt(II) coordination center in **Pt-BDP** can be attributed to TTET to the BDP moiety because PET is also prohibited in this case.

The excitation spectra of **Pt-BDP** and **Pt-Ph** are compared with the UV-vis absorption spectra (Figure 5).<sup>78-80</sup> The



**Figure 5.** Comparison of the normalized UV–vis absorption and luminescence excitation spectra of (a) **Pt-BDP** ( $\lambda_{em} = 650 \text{ nm}$ ) and (b) **Pt-Ph** ( $\lambda_{em} = 650 \text{ nm}$ ).  $c = 1.0 \times 10^{-5} \text{ M}$  in degassed toluene, 20 °C.

phosphorescence emission of the Pt(II) coordination center at 650 nm in **Pt-BDP** and **Pt-Ph** was monitored in the excitation spectra. Both complexes show decreased excitation bands above 400 nm compared to the UV–vis absorption spectrum (with normalization at the absorption maximum, ca. 570 nm). Similar phenomena have been observed for naphthalenediimide and perylenebisimide chromophores.<sup>81–83</sup>

Besides the change at higher-energy bands, **Pt-BDP** shows a comparably large excitation peak at 503 nm, which corresponds to the absorption band of the BDP moiety (Figure 5a). Because the Pt(II) coordination center and BDP moiety have almost no electronic interaction, phosphorescence emission of the Pt(II) coordination center upon excitation of BDP clearly indicates FRET from BDP to the Pt(II) coordination center. The FRET efficiency is estimated to be approximately 47%.<sup>78</sup>

The singlet-oxygen  $({}^{1}O_{2})$  photosensitizing ability of the complexes was studied (Table 1; for details, see Figure S15). 1,3-Diphenylisobenzofuran was used as an  ${}^{1}O_{2}$  scavenger for monitoring  ${}^{1}O_{2}$  production. Given that no intramolecular energy transfer occurred, photoexcitation of **Pt-BDP** at 500 nm

will not show significant  ${}^{1}O_{2}$  photosensitizing because the absorption band at 500 nm corresponds to BDP excitation. However, the results show that **Pt-BDP** gives  ${}^{1}O_{2}$  quantum yields ( $\Phi_{\Delta}$ ) of 77% upon photoexcitation at 500 nm, similar to **Pt-Ph** (Table 1). Thus, we can deduce that singlet energy transfer would occur upon excitation of the BDP moiety in **Pt-BDP**, followed by a TTET that would finally localize the triplet state on the BDP unit.

**Time-Resolved Photoluminescence Spectroscopy.** For BDP, a luminescence decay with a monoexponential profile was observed (Figure 6a), with the lifetime determined as 3.8 ns;



**Figure 6.** (a) Fluorescence decay curves of **Pt-BDP** ( $\lambda_{em} = 515$  nm) and BDP (500 nm). Excited with a 445 nm picosecond pulsed laser. (b) Phosphorescence decay curves of **Pt-BDP** ( $\lambda_{em} = 650$  nm) and **Pt-Ph** ( $\lambda_{em} = 650$  nm). Excited with a 445 nm picosecond pulsed laser;  $c = 1.0 \times 10^{-5}$  M in deaerated toluene, 20 °C.

this is assigned as the  $S_1$  state lifetime. For **Pt-Ph**, the phosphorescence lifetime was determined to be 3.7  $\mu$ s, also with a monoexponential decay feature (Figure 6b).

On the other hand, for **Pt-BDP**, the *fluorescence* decay of the BDP moiety is with biexponential character of 0.085 ns (ca. 99%) and 4.8 ns (ca. 1%). Because the BDP moiety is far away from the Pt(II) center (9.4 Å), the  $\pi$  core of the BDP fluorophore is not  $\pi$ -conjugated with the coordination center and PET is thermodynamically inhibited (see the later section). Thus, we propose that the main fluorescence-quenching pathway is FRET from the BDP moiety to the Pt(II) coordination center. On the basis of the fs-TA spectral changes, i.e., growing in of the spectral features associated with the Pt(II) center and decay of the BDP-based absorbance, we calculate the FRET rate constant to be  $k_{\text{FRET}} = 1.5 \times 10^{11} \text{ s}^{-1}$  (see the fs-TA study section).

In the case of *phosphorescence* (Figure 6b), we attribute the quenched phosphorescence of the Pt(II) coordination center in **Pt-BDP** to intramolecular TTET from the Pt(II) coordination center to the BDP moiety. The shorter phosphorescence lifetime at the Pt(II) coordination center of **Pt-BDP** (18.3 ns/ 98% and 3.9  $\mu$ s/2%), compared to **Pt-Ph** (3.7  $\mu$ s), indicates the existence of quenching channels for the emissive triplet state of the Pt(II) coordination center, presumably TTET.

The photophysical properties of **Pt-BDP**, **Pt-Ph**, and BDP are compiled in Table 1. The  ${}^{1}O_{2}$  quantum yield ( $\Phi_{\Delta}$ ) of **Pt-BDP** is as high as 77% ( $\lambda_{ex} = 500 \text{ nm}$ ), and the quantum yield of triplet formation in **Pt-BDP** is  $\Phi_{T} = 89\%$  ( $\lambda_{ex} = 532 \text{ nm}$ ).

Electrochemical Study: Gibbs Free-Energy Changes ( $\Delta G_{CS}$ ) of PET and the Charge-Separated State (CSS) Energy Levels. The redox properties of the complexes are studied using cyclic voltammetry (Figure 7). For Pt-Ph, a reversible oxidation wave was observed, and the half-wave potential ( $E_{1/2}$ ) is +0.61 V. A reversible reduction is observed with  $E_{1/2}$  of -1.83 V (Figure 7b). For Pt-BDP, reversible



Figure 7. Cyclic voltammograms of (a) Pt-BDP and BDP and (b) Pt-BDP and Pt-Ph. Ferrocene ( $Fc^{0/+}$ ) is used as an internal reference. In degassed CH<sub>2</sub>Cl<sub>2</sub> solutions containing 1.0 mM photosensitizers and Fc (0.5 mM), 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> is the supporting electrolyte and Ag/AgNO<sub>3</sub> is the reference electrode. Scan rate: 50 mV s<sup>-1</sup>. T = 20 °C.

reduction waves were observed, and the  $E_{1/2}$  values are -1.53 and -1.86 V, respectively. Reversible oxidation waves were observed, with potentials of +0.63 and +0.80 V, respectively (Figure 7b). This result indicates that there is no electronic interaction between the two units in **Pt-BDP**; otherwise, the redox potentials of **Pt-BDP** would be different from those of the reference compounds (Table 2).

$$\Delta G_{\rm CS} = e[E_{\rm OX} - E_{\rm RED}] - E_{00} + \Delta G_{\rm S} \tag{1}$$
$$\Delta G_{\rm S} = -\frac{e^2}{4\pi\varepsilon_{\rm S}\varepsilon_{\rm 0}R_{\rm CC}} - \frac{e^2}{8\pi\varepsilon_{\rm 0}} \left(\frac{1}{R_{\rm D}} + \frac{1}{R_{\rm A}}\right) \left(\frac{1}{\varepsilon_{\rm REF}} - \frac{1}{\varepsilon_{\rm S}}\right) \tag{2}$$

Table 2. Electrochemical Redox Potentials of Pt-BDP, Pt-Ph, and  $BDP^{a}$ 

compound	$E_{\rm OX}/{\rm V}$	$E_{\rm RED}/{ m V}$
Pt-BDP	+0.80, +0.63	-1.53, -1.86
Pt-Ph	+0.61	-1.83
BDP	+0.76	-1.55

<sup>*a*</sup>Cyclic voltammetry in Ar-saturated CH<sub>2</sub>Cl<sub>2</sub> containing a 1.0 mM photosensitizer and a 0.10 M Bu<sub>4</sub>N[PF<sub>6</sub>] supporting electrolyte. A Pt counter electrode, a glassy carbon working electrode, and an Ag/AgNO<sub>3</sub> reference electrode were used. Fc was used as an internal reference. Scan rate: 50 mV s<sup>-1</sup>. T = 20 °C.

To study the possibility of intramolecular PET, the  $\Delta G_{CS}$ values of **Pt-BDP** in several solvents were calculated using the Weller equation (eqs 1 and 2).<sup>84–87</sup>  $\Delta G_{\rm S}$  is the static Coulombic energy (eq 2), where e = electronic charge,  $E_{OX}$  is the half-wave potential for one-electron oxidation of the electron-donor unit (+0.58 V),  $E_{\text{RED}}$  is the half-wave potential for one-electron reduction of the electron-acceptor unit (-1.57)V),  $E_{00}$  is the energy level for the singlet excited state approximated by the fluorescence emission (510 nm and 2.43 eV) or the triplet excited state approximated with the phosphorescence emission (562 nm and 2.21 eV),  $\varepsilon_{\rm S}$  is the static dielectric constant of the solvent, R<sub>CC</sub> is the center-tocenter separation distance determined by density functional theory (DFT) optimization of the geometry (10.63 Å),  $R_{\rm D}$  is the radius of the electron donor (4.36 Å),  $R_A$  is the radius of the electron acceptor (6.86 Å),  $\varepsilon_{\rm S}$  is the static dielectric constant of the solvent used for electrochemical studies, and  $\varepsilon_0$  is the permittivity of free space. The solvents used are toluene ( $\varepsilon_{\rm S}$  = 2.4), CH<sub>2</sub>Cl<sub>2</sub> ( $\varepsilon_{s}$  = 8.9), and CH<sub>3</sub>CN ( $\varepsilon_{s}$  = 37.5). The energies of the CSS  $(E_{CS})$  and the free-energy change of the charge

# Table 3. Free-Energy Changes of Pt-BDP: $\Delta G_{CS}$ , $E_{CSS}$ , and $\Delta G_{S}^{a}$

<sup>*a*</sup>The arrow indicates the direction of charge transfer. <sup>*b*</sup>Electron donor. <sup>*c*</sup>Electron acceptor. <sup>*d*</sup>Energy level of the triplet state of BDP as  $E_{00}$ . <sup>*e*</sup>Energy level of the singlet state of BDP as  $E_{00}$ .

recombination process ( $\Delta G_{CR}$ ) are calculated using eqs 3 and 4.

 $E_{\rm CS} = e[E_{\rm OX} - E_{\rm RED}] + \Delta G_{\rm S} \tag{3}$ 

$$\Delta G_{\rm CR} = -(\Delta G_{\rm CS} + E_{00}) \tag{4}$$

The Gibbs free-energy changes for putative electron transfer are positive (Table 3), indicating that the intramolecular PET in **Pt-BDP** and **Pt-Ph** is thermodynamically unfavorable. This conclusion agrees well with the luminescence emission spectra and triplet-state study of the complexes.

fs-TA Spectroscopy: Intramolecular Singlet-Triplet Energy Transfer (Ping-Pong Energy Transfer). To investigate the excited-state dynamics of the Pt-BDP complex, fs-TA measurements were carried out (Figure 8). First, the



**Figure 8.** fs-TA spectra of **Pt-BDP** (a) from 1 to 20 ps and (b) from 30 ps to 5 ns. (c) SADS spectra obtained by global target analysis. In toluene (490 nm excitation).

complex **Pt-BDP** was excited at 490 nm, which corresponds to the  $S_0 \rightarrow S_1$  transition of the BDP ligand. From 1 to 20 ps, we observed a decay of the ground-state bleach (GSB) band of the BDP moiety at 510 nm and a simultaneous rise in the excitedstate absorption (ESA) band in the 600–700 nm region. These spectral changes are ascribed to FRET from the BDP moiety to the Pt–Schiff base coordination framework. After the initial spectral evolution, from 30 ps to 5 ns, we observed a rise in the BDP GSB band at 510 nm and the ESA band at ca. 640 nm, which corresponds to the spectral features of the BDP-moietylocalized T<sub>1</sub> state, as observed in ns-TA studies (see the ns-TA section). This process is a TTET from the  $T_1$  state of the Pt coordination center to the  $T_1$  state of the BDP moiety. However, ISC in the Pt(II) coordination center of **Pt-BDP** was not observed, presumably because it is extremely fast, similar to other Pt–Schiff base complexes that exhibit subpicosecond ISC time constants.<sup>88</sup> This ultrafast ISC process at the Pt–Schiff base is further supported by the fs-TA spectra of **Pt-Ph** upon photoexcitation at 560 nm (Figure S17), which shows the ultrafast evolution of the  $T_1$  state spectral features of **Pt-Ph** within 1 ps.

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Using a global target analysis assuming four states [the  $S_1$  state of BDP,  $S_1$  and  $T_1$  states of the Pt(II)–Schiff base complex, and  $T_1$  state of BDP] that are involved in the excited-state dynamics, consecutively, and assuming that ISC at the Pt–Schiff base coordination framework and TTET are too fast for the  $S_1$  and  $T_1$  states of the Pt–Schiff base to be resolved, we can extract the species-associated difference spectroscopy (SADS) spectra of each state and the rate constants of the FRET and TTET processes (Figure 8c and Table 4). Species A shows a

Table 4. FRET, TTET, and ISC Rate Constants of the Complexes Using Ultrafast TA Spectroscopy (in Toluene)

compound	$k_{\rm FRET}^{a}/{\rm s}^{-1}$	$k_{\text{TTET}}^{}b}/\text{s}^{-1}$
Pt-BDP	$1.5 \times 10^{11}$	$6.8 \times 10^{9}$
Pt-Ph		

<sup>a</sup>FRET rate constants. <sup>b</sup>TTET rate constants.

strong GSB at 510 nm and a relatively weak ESA, which is assigned to the S<sub>1</sub> state of BDP, while species B is assigned to the T<sub>1</sub> state of the Pt-Schiff base coordination center because it shows spectral features similar to those of the T1 state of Pt-Ph observed in the ns-TA spectra (see the ns-TA section). Thus, the spectral change  $A \rightarrow B$  represents a FRET process from the S<sub>1</sub> state of the BDP moiety to that of the Pt-Schiff base coordination framework with a time constant of 6.7 ps  $(k_{\text{ERET}} = 1.5 \times 10^{11} \text{ s}^{-1})$ , followed by ultrafast ISC in the Pt-Schiff base coordination framework. Species C corresponds to the  $T_1$  state of the BDP moiety, which can be identified by the resolved spectrum being similar to the T1 state of the BDP moiety (see the ns-TA section). Therefore, process  $B \rightarrow C$ represents triplet-triplet back-energy transfer from the T<sub>1</sub> state of the Pt-Schiff base framework to the T<sub>1</sub> state of the BDP moiety with a time constant of 148 ps ( $k_{\text{TTET}} = 6.8 \times 10^9 \text{ s}^{-1}$ ).

Next, the excitation wavelength is tuned to 560 nm, corresponding to the  $S_0 \rightarrow S_1$  transition of the Pt(II)–Schiff base coordination framework (Figure 9a). From 1 ps to 5 ns, we observed a rise in the GSB band of the BDP moiety at 510 nm and a simultaneous decay of the ESA band of the complex at 600–700 nm. This spectral change can be ascribed to TTET from the  $T_1$  state of the Pt–Schiff base complex to that of the BDP moiety. Because of the fast time constant, the ISC of the

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**Figure 9.** (a) fs-TA spectra measured from 1 ps to 5 ns for **Pt-BDP** in toluene (560 nm excitation). (b) SADS spectra of **Pt-BDP** in toluene obtained by global target analysis.

Pt(II) coordination center in **Pt-BDP** was not observable at 560 nm.

Furthermore, by using a global target analysis assuming that three states (the S<sub>1</sub> and T<sub>1</sub> states of the Pt(II) coordination center and T<sub>1</sub> state of the BDP moiety) are involved in the excited-state dynamics, the generation of these states is in a consecutive order, and because the ISC process in the Pt– Schiff base is ultrafast, we can extract the SADS spectrum of each state and the ISC rate constants (Figure 9b and Table 4). Species B and C can be assigned as the S<sub>1</sub> state of the Pt–Schiff base complex and the T<sub>1</sub> state of the BDP moiety, respectively, because they show SADS spectra almost identical with those of species B and C obtained at 490 nm. Therefore,  $B \rightarrow C$ represents TTET in the Pt–Schiff base complex with a time constant of 143 ps ( $k_{\text{TTET}} = 7.0 \times 10^9 \text{ s}^{-1}$ ), following the ultrafast ISC of the Pt(II)–Schiff base coordination center.

**ns-TA Spectroscopy.** To study the triplet-state properties, i.e., the lifetime and spatial localization of the triplet state of the complexes, the ns-TA spectra of **Pt-Ph** and **Pt-BDP** were measured (Figure 10). For **Pt-Ph**, upon pulsed-laser excitation at 532 nm, GSB bands at 391 nm as well as broad ESA bands in the range of 400–700 nm were observed (Figure 10a). The lifetime of this transient signal is measured to be 3.5  $\mu$ s (Figure 10b) in degassed solutions and 0.5  $\mu$ s in aerated solutions (Figure S18). From the significantly reduced lifetime in aerated solutions, we can assign this transient signal as the triplet state of **Pt-Ph**.

For **Pt-BDP**, an intense GSB band at 504 nm was observed upon nanosecond pulsed-laser excitation at 532 nm (Figure 10c). This excitation wavelength corresponds to the  $S_0 \rightarrow S_1$ transition of the Pt(II)–Schiff base coordination center; however, the resulting transient signal corresponds to the  $T_1$ state of the BDP moiety, as identified by a GSB band at 504 nm, which corresponds to the ground-state absorption of BDP (Figure 10c). Furthermore, the ESA bands also agree with absorption of the BDP triplet state reported previously.<sup>89–91</sup> This result further supports fast TTET from the Pt(II) coordination center to the BDP moiety, as observed in fs-TA studies. The triplet-state lifetime was determined to be 103.2  $\mu$ s, which is much longer than the BDP triplet state accessed with the heavy-atom effect, such as in 2,6-diiodoBDP (57.1  $\mu$ s).<sup>44</sup> This implies that the heavy-atom effect from the Pt–



**Figure 10.** Time-resolved ns-TA spectra: (a) **Pt-Ph**, (b) decay trace of **Pt-Ph** at 391 nm, (c) **Pt-BDP**, and (d) decay trace of **Pt-BDP** at 504 nm.  $\lambda_{ex} = 532$  nm laser.  $c = 1.0 \times 10^{-5}$  M in degassed toluene, 20 °C.

Schiff base complex exerted on the BDP unit is not very significant.

The photophysical process of **Pt-BDP** is summarized in Scheme 2. Upon selective excitation of the BDP moiety, FRET





<sup>a</sup>Note the ping-pong energy-transfer processes.

from the BDP moiety to the Pt–Schiff base complex occurs. This is followed by fast ISC at the Pt–Schiff base complex. Backward TTET from the Pt–Schiff base complex to the BDP moiety is observed with a time constant of ca. 140 ps. Thus, we can conclude that the  $T_1$  state of complex **Pt-BDP** is exclusively localized on the BDP moiety.

**DFT Calculations.** The photophysical properties of the complex are rationalized with DFT and time-dependent DFT (TDDFT) calculations (Figure 11). We find that the molecular orbitals are highly localized, on either the Pt(II) center or the BDP moiety. This result is in accordance with the spectroscopic measurements. There are almost no electronic interactions between the two moieties in the ground state. The lowest singlet state (S<sub>1</sub> state, HOMO  $\rightarrow$  LUMO+1) of **Pt-BDP** is localized on the Pt(II) coordination framework, and the calculated transition energy of 2.29 eV (542 nm) is close to the experimental values (2.17 eV and 530 nm). The lowest-energy transition between the singlet states localized on the BDP moiety is the S<sub>0</sub>  $\rightarrow$  S<sub>6</sub> transition (HOMO-1  $\rightarrow$  LUMO), with



**Figure 11.** Electron density maps of the frontier molecular orbitals of **Pt-BDP**, calculated using DFT at the B3LYP/GENECP/LANL2DZ level with *Gaussian 09W*.

an excitation energy of 2.86 eV (433 nm), which is higher than the experimental value of 530 nm (Figure 11). The calculated energy is higher than the experimental value, which can be explained by well-known reports that the DFT method usually overestimates the excitation energy for BDP chromophores.<sup>92–94</sup>

For the  $T_3$  state (2.01 eV) localized on the Pt(II) coordination center, it is close in energy to the coordinationcenter-localized  $S_1$  state (2.29 eV). The small energy difference between the  $S_1$  and  $T_3$  states shows the possibility for fast ISC between the two states. Interestingly, the lowest excited triplet state ( $T_1$  state) is a BDP-localized state; thus, nonradiative fast internal conversion  $T_3 \rightarrow T_1$  may occur, which corresponds to the intramolecular TTET process from the Pt(II) coordination center to BDP. The heavy-atom effect for this BDP-localized triplet state is confirmed to be weak because there are only small electronic interactions between BDP and the Pt(II) coordination center. This has been proven both spectroscopically and computationally. Detailed information on the excitedstate energy levels and electronic configurations is presented in Table S2.

To determine where the lowest-energy triplet states are localized in **Pt-BDP** and **Pt-Ph**, the spin-density surfaces of these complexes are calculated (Figure 12). The spin-density surface of **Pt-Ph** is mainly distributed on the Schiff base ligand, the Pt(II) metal center, and the pendent phenyl ring. This calculation agrees with the MLCT/IL state feature. For **Pt-BDP**, on the other hand, the spin-density surface is exclusively localized on the BDP moiety, in accordance with the ns-TA results, which proposes a long-lived triplet state localized at BDP in **Pt-BDP**.

TTA Upconversion: Benefit of Ping-Pong Energy Transfer for Attaining a Large Anti-Stokes Shift. Complexes Pt-BDP and Pt-Ph are examined as triplet photosensitizers for TTA upconversion (Figure 13). On the



**Figure 13.** TTA upconversion with (a) **Pt-BDP** and (b) **Pt-Ph** as triplet photosensitizers ( $c = 1.0 \times 10^{-5}$  M) and perylene as the triplet acceptor ( $c = 4.0 \times 10^{-5}$  M) in degassed toluene, 25 °C. P stands for photoexcitation of both **Pt-BDP** and **Pt-Ph** at 510 and 589 nm without perylene. P1 stands for photoexcitation at 589 nm with the addition of perylene. P2 stands for photoexcitation at 510 nm with the addition of perylene. P3 stands for simultaneous photoexcitation with 510 and 589 nm using a 4 mW continuous-wave (cw) laser (the two laser beams are in quasi-collinear geometry) with the addition of perylene. Asterisks indicate laser scattering.



Figure 12. Spin-density surfaces of (a) Pt-Ph and (b) Pt-BDP at the optimized triplet-state geometry calculated at the B3LYP/GENCEP/LANL2DZ level with *Gaussian 09W*.

basis of the excited-state energy levels of the complexes, we select perylene as the triplet acceptor/emitter for the upconversion studies.<sup>44,91</sup> The excitation wavelength was selected as 510 and 589 nm, which correspond to the  $S_0 \rightarrow S_1$  transition of the BDP moiety and the Pt(II)–Schiff base coordination framework, respectively.

The upconversion quantum yields of **Pt-Ph** and **Pt-BDP** were calculated from the upconverted fluorescence with 510 and 589 nm excitation (Table 5 and Figure 13). For **Pt-Ph**,

Table 5. Triplet Excited-State Lifetimes ( $\tau_{\rm T}$ ), Stern–Volmer Quenching Constant ( $K_{\rm SV}$ ), and Bimolecular Quenching Constant ( $K_{\rm q}$ ) of Pt-BDP and Pt-Ph in Degassed Toluene at 20 °C

	$ au_{ m T}/\mu{ m s}$	$\frac{K_{\rm SV}}{{ m M}^{-1}}$	$k_{q}^{b}/\times 10^{8}$ M <sup>-1</sup> s <sup>-1</sup>	$\frac{k_0^{\ c}}{M^{-1} \ s^{-1}}$	${\Phi_{ m UC}}^d/\%$	f <sup>g</sup> /%
Pt- BDP	107.7 <sup>a</sup>	8.3	7.8	1.46	10.0 <sup>e</sup> / 1.0 <sup>f</sup>	5.34
Pt-Ph	3.87 <sup>a</sup>	0.3	7.8	1.25	$2.0^{e}/$ $0.02^{f}$	6.24

"Excited with a 532 nm cw laser. <sup>b</sup>Bimolecular quenching constant.  $K_{SV} = k_q \tau_0$ . <sup>c</sup>Diffusion-controlled bimolecular quenching rating constant. <sup>d</sup>Upconversion quantum yields. <sup>e</sup>Excited with a 510 nm cw laser (4 mW), with 2,6-diiodoBDP as the standard ( $\Phi_F = 3.6\%$  in CH<sub>2</sub>Cl<sub>2</sub>). <sup>f</sup>Excited with a 589 nm cw laser (4 mW), with styrylBDP as the standard ( $\Phi_F = 59\%$  in CH<sub>2</sub>Cl<sub>2</sub>). <sup>g</sup>Quenching efficiency.

barely any upconversion was observed and the upconversion quantum yields were determined as 2% and 0.02% at the two excitation wavelengths, respectively. On the other hand, under the same conditions (laser power, photosensitizer concentration, and triplet acceptor), the upconversion quantum yields with **Pt-BDP** as the triplet photosensitizer were measured to be 10% and 1%, respectively, which are almost 5 times higher than those of **Pt-Ph**. The upconversion of **Pt-BDP** is clearly visible to the unaided eye (Figure 14).



**Figure 14.** Photographs of the emissions of triplet photosensitizers alone and TTA upconversion: (a) TTA upconversion with **Pt-BDP** and **Pt-Ph** excited with a 510 nm laser. (b) CIF diagram of the upconversion with 510 nm laser excitation. (c) TTA upconversion with **Pt-BDP** and **Pt-Ph** at 589 nm laser excitation. (d) CIF diagram of the upconversion with 589 nm laser excitation with **Pt-BDP** and **Pt-Ph** as the triplet photosensitizers ( $c = 1.0 \times 10^{-5}$  M) and perylene (Py) as the acceptor ( $4.0 \times 10^{-5}$  M). Excited with a 4 mW cw laser ( $\lambda_{ex} = 510$  and 589 nm), 20 °C in toluene.

It should be pointed out that a large anti-Stokes shift in the TTA upconversion can also be achieved with other molecular systems, for instance, those based on the combination of a perylene acceptor and benzoporphyrin sensitizers having rather small  $S_1/T_1$  state energy gaps.<sup>95</sup> However, the large anti-Stokes shifts of the TTA upconversion of the current molecular systems are based on excited-state tuning of the triplet photosensitizer; i.e., the  $T_1$  state of the BDP ligand was kept, but the excitation wavelength was red-shifted by attachment of the Pt(II) center and the FRET in the complex.

Excitation with the quasi-collinear geometry of 510/589 nm laser beams, i.e., the simultaneous excitation with a two-color laser, was also studied for **Pt-Ph** and **Pt-BDP** (Figure 13). Interestingly, the upconversion intensity is measured to be roughly the sum of the upconversions upon excitation by a 510 or 589 nm laser individually.

To study the origin of the efficient upconversion with Pt-BDP as a triplet photosensitizer versus that with Pt-Ph, the intermolecular TTET between the Pt(II) complexes and perylene was studied with triplet-state lifetime changes in the complexes in the presence of perylene (Table 5 and Figure 15).



**Figure 15.** Stern–Volmer plots generated from the triplet excited-state lifetime ( $\tau_{\rm T}$ ) quenching curves of **Pt-BDP** ( $c = 1.0 \times 10^{-5}$  M) and **Pt-Ph** ( $c = 1.0 \times 10^{-5}$  M) measured with increasing concentrations of perylene ( $c = 1.0 \times 10^{-5}$  M). The triplet-state lifetime of the complexes is measured with a 532 nm nanosecond-pulsed-laser excitation in degassed toluene at 20 °C.

Note that **Pt-BDP** shows a 28 times larger Stern–Volmer quenching constant than that of **Pt-Ph** ( $K_{sv} = 8.3 \times 10^4 \text{ M}^{-1}$  for **Pt-BDP** and  $K_{sv} = 0.3 \times 10^4 \text{ M}^{-1}$  for **Pt-Ph**). This can be attributed to the longer triplet-state lifetime of **Pt-BDP** due to localization of the triplet state on the BDP unit, which is crucial for an efficient upconversion.

Interestingly, the anti-Stokes shift for the upconversion with **Pt-BDP** at 589 nm excitation increases to 0.65 eV, which is comparable to a previously reported 0.86 eV for an  $Os^{II}(bpy)_3$  complex showing a large anti-Stokes shift.<sup>43</sup> However, the reported  $Os^{II}(bpy)_3$  complex shows very low upconversion yields in the solution phase ( $\Phi_{UC} = 0.0014\%$ ), at a very high excitation power density (212 W cm<sup>-2</sup>) because of its small extinction coefficient and short triplet-state lifetime ( $\varepsilon = 3200$   $M^{-1}$  cm<sup>-1</sup> at 888 nm for the  $S_0 \rightarrow T_1$  transition and  $\tau_T = 12$  ns).<sup>43</sup> In contrast, **Pt-BDP** shows a higher upconversion yield, reaching 1%. The upconversion quantum yield of **Pt-BDP** is even higher than the previously reported sensitizers excited with near-IR light (<1%), which also have comparable anti-Stokes shifts of 0.70 and 0.86 eV.<sup>37</sup>

Herein with **Pt-BDP**, we propose a new method to obtain TTA upconversion from a broad-band light source, high upconversion quantum yields, and large anti-Stokes shift utilizing ping-pong energy transfer. By linking a Pt–Schiff

base coordination framework to the BDP moiety, we can efficiently generate a triplet state localized in the BDP moiety over a wide range of visible-light sources through efficient ISC and TTET. A large anti-Stokes shift can be obtained by excitation at 589 nm, where the Pt(II) coordination center only absorbs moderately. In this case, an anti-Stokes shift up to 5290 cm<sup>-1</sup> (0.65 eV) is obtained, which is larger than the anti-Stokes shift obtained by excitation of the BDP moiety (2660 cm<sup>-1</sup>, 0.33 eV), with perylene as the triplet acceptor/emitter.

# CONCLUSIONS

In summary, we prepared a Pt(II)-Schiff base complex with a BDP moiety attached to the Schiff base ligand. The photophysical properties of the complex and reference compounds were studied with steady-state UV-vis absorption, luminescence spectroscopy, time-resolved fs/ns-TA spectroscopies, and cyclic voltammetry and DFT/TDDFT calculations. The ultrafast intramolecular singlet-triplet energy transfer in Pt-BDP was observed using fs-TA spectroscopy. A forward singlet energy transfer from the BDP moiety to the Pt(II) coordination center (FRET,  $k_{\text{FRET}} = 1.5 \times 10^{11} \text{ s}^{-1}$ ) is accompanied by an ultrafast ISC (<1 ps, confirmed with Pt-Ph) at the Pt(II) coordination center and a backward TTET from the Pt(II) coordination center to the BDP moiety (TTET,  $k_{\text{TTET}} = 6.8 \times 10^9 \text{ s}^{-1}$ ). Localization of the triplet state at BDP upon excitation of Pt-BDP is confirmed by ns-TA spectroscopy. **Pt-BDP** has a longer triplet-state lifetime  $(\tau_{\rm T})$  of 103.2  $\mu$ s compared to the reference complex Pt-Ph, which shows a triplet state localized mainly on the Pt(II)-Schiff base coordination center with  $\tau_{\rm T}$  = 3.5  $\mu$ s. Finally, **Pt-BDP** is examined as a triplet photosensitizer for TTA upconversion. We find that the complex shows high upconversion quantum yields upon excitation of BDP, up to 10%, and a large anti-Stokes shift upon excitation of the lowest absorption band (increased to  $5290 \text{ cm}^{-1}$ , 0.65 eV). We propose the use of triplet photosensitizers showing ping-pong energy transfer as a method to increase the anti-Stokes shift of TTA upconversion.

### EXPERIMENTAL SECTION

**Materials.** Solvents were dried or distilled before use.  $K_2PtCl_4$  was purchased from Aladdin Chemical Co., Ltd. (China). Compounds 1, 2, Pt-BDP, and Pt-Ph were prepared according to literature procedures.<sup>58</sup>

Analytical Measurements. NMR spectra were recorded on a Bruker 400 MHz spectrometer with  $CDCl_3$  or dimethyl sulfoxide (DMSO)- $d_6$  as solvents. HRMS was determined using a TOF MALDI HRMS system (U.K.). Fluorescence spectra were measured on a RF5301 PC spectrofluorometer (Shimadzu, Japan) and a FS5 spectrofluorometer (Edinburgh Instruments, U.K.). UV–vis absorption spectra were recorded on a UV2550 UV–vis spectrophotometer (Shimadzu, Japan).

Synthesis of **Pt-BDP**. Under an Ar atmosphere, **2** (80.0 mg, 0.10 mmol), **4** (112.0 mg, 0.15 mmol), Na<sub>2</sub>CO<sub>3</sub> (65.0 mg, 0.45 mmol), and solvents of ethanol (EtOH)/toluene/water (20 mL, 2:4:1, v/v/v) were mixed. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (9.0 mg, 0.007 mmol, 5 mol %) was added. The reaction mixture was refluxed and stirred under an Ar atmosphere for 8 h. After the reaction was complete, the mixture was cooled to room temperature, then extracted with CH<sub>2</sub>Cl<sub>2</sub>, and washed with water (2 × 100 mL), and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was evaporated to dryness under reduced pressure to give a crude solid, which was further purified with column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to yield **Pt-BDP** as a red solid (32 mg, yield 38%). Mp: >250 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  9.01 (s, 1H), 8.93 (s, 1H), 8.23 (s, 1H), 8.11 (d, 1H, *J* = 8.0 Hz), 7.89 (d, 2H, *J* = 8.0 Hz), 7.69 (s, 2H), 7.64 (d, 1H, *J* = 12.0 Hz), 7.47

(d, 2H, *J* = 8.0 Hz), 7.40 (s, 1H), 7.36 (s, 1H), 6.02 (s, 2H), 2.58 (s, 6H), 1.60 (s, 18H), 1.50 (s, 6H), 1.37 (s, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  164.5, 155.8, 148.5, 148.4, 145.8, 143.0, 141.6, 138.6, 137.8, 134.8, 131.4, 129.0, 127.7, 125.4, 121.4, 120.8, 115.1, 113.1, 36.2, 34.0, 31.3, 29.7. TOF MALDI HRMS. Calcd ([ $C_{55}H_{63}BF_2N_4O_2Pt$ ]<sup>+</sup>): *m/z* 1055.4660. Found: *m/z* 1055.4642.

Synthesis of Pt-Ph. Under an Ar atmosphere, 2 (80.0 mg, 0.10 mmol), phenylboronic acid (18.0 mg, 0.15 mmol), K<sub>2</sub>CO<sub>3</sub> (42.0 mg, 0.30 mmol), and EtOH/toluene/water (20 mL, 2:4:1, v/v/v) were mixed together. Then,  $Pd(PPh_3)_4$  (9.0 mg, 0.007 mmol, 5 mol %) was added. The mixture was refluxed and stirred under an Ar atmosphere for 10 h. Then the mixture was cooled to room temperature. The reaction mixture was extracted with  $CH_2Cl_2$ , washed with water (2 × 100 mL), and dried over anhydrous Na2SO4. The solution was evaporated to dryness under reduced pressure to give a crude solid, which was further purified with column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) to yield Pt-Ph as a dark red solid (38 mg, yield 40%). Mp: >200 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.92 (s, 1H), 8.87 (s, 1H), 8.10 (s, 1H), 8.03 (d, 1H, J = 8 Hz), 7.69 (d, 4H, J = 8.0 Hz), 7.52 (t, 3H, J<sub>1</sub> = 4 Hz, J<sub>2</sub> = 8 Hz,), 7.44 (t, 1H, J<sub>1</sub> = 8 Hz, J<sub>2</sub> = 4 Hz), 7.34 (d, 2H, J = 8.0 Hz), 1.59 (s, 18H), 1.36 (s, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): *δ* 164.4, 164.3, 148.5, 145.6, 144.5, 141.5, 140.1, 139.6, 137.6, 131.0, 129.0, 127.1, 125.6, 120.8, 115.0, 113.2, 36.3, 34.1, 31.3, 29.5. TOF MALDI HRMS. Calcd  $([C_{42}H_{50}N_2O_2Pt]^+): m/z 810.3598.$ Found: m/z 810.3570.

**X-ray Crystallography.** Pt-Ph (20 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) in small test tube, and hexane (6 mL) was added slowly. After a few days of slow evaporation of the solvent at room temperature, red needlelike crystals were obtained, and the crystals were used for single-crystal X-ray diffraction analysis. The crystal data of **Pt-Ph** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source; the data were acquired using the *SMART* and *SAINT* programs. The structure was solved by direct methods and refined on  $F^2$  using full-matrix least-squares methods by the *SHELXTL*, version 5.1, software.<sup>96</sup> The non-H atoms were refined anisotropically. Crystal data and details of the data collection and structural refinements for **Pt-Ph** are summarized in Table S1.

Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information can be obtained free of charge by quoting the deposition number CCDC 1565649 (Pt-Ph).

**Cyclic Voltammetry.** Cyclic voltammetry was measured using a CHI610D electrochemical workstation (CH instruments, Inc., Shanghai, China). Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N-[PF<sub>6</sub>], 0.1 M) was used as the supporting electrolyte, and glassy carbon and platinum electrodes were used as the working and counter electrodes, respectively. CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent. Fc was used as the internal reference. The solution was purged with N<sub>2</sub> before the measurements, and the N<sub>2</sub> gas flow was maintained during the measurements. The measurements were performed under a 50 mV s<sup>-1</sup> scan rate at room temperature.

**ns-TA Spectroscopy.** The ns-TA spectra were recorded on an LP920 laser flash photolysis spectrometer (Edinburgh Instruments, U.K.). The signal was digitized with a Tektronix TDS 3012B oscilloscope. All samples were purged with  $N_2$  for 15 min before the measurements and excited with an Opolette 355II+UV nanosecond pulse laser. The data were processed with the LP900 software.

**fs-TA Spectroscopy.** The ultrafast TA (pump-probe) spectroscopy measurements were performed using a Ti:sapphire laser amplifier-optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) and a commercial ultrafast TA spectrometer setup (Spectra Physics, Helios). The pulse duration was 100 fs. Wavelengths of the pump beam were chosen according to the steady-state absorption spectra of the studied compounds. A white-light continuum was generated with the sapphire crystal and used as the probe beam.

**DFT Calculations.** Geometry optimizations were carried out using the B3LYP functional with 6-31G(d) basis sets for the C, H, O,<sup>97</sup> and N elements and the LANL2DZ basis set for the Pt atom,<sup>98</sup> while the

vertical excitation energy was calculated with the TDDFT method based on the singlet ground-state geometry.<sup>99</sup> All calculations were performed with the *Gaussian 09W* software (Gaussian, Inc.).<sup>100</sup>

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02989.

<sup>1</sup>H and <sup>13</sup>C NMR data, HRMS and photophysical spectra, and DFT/TDDFT calculations of the complexes (PDF)

#### Accession Codes

CCDC 1565649 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

We thank the NSFC (Grants 21473020, 21673031, 21761142005, 21603021, 21421005, and 21273028), the State Key Laboratory of Fine Chemicals (ZYTS201801), and the Fundamental Research Funds for the Central Universities (Grants DUT16TD25, DUT15ZD224, and DUT2016TB12) for financial support.

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