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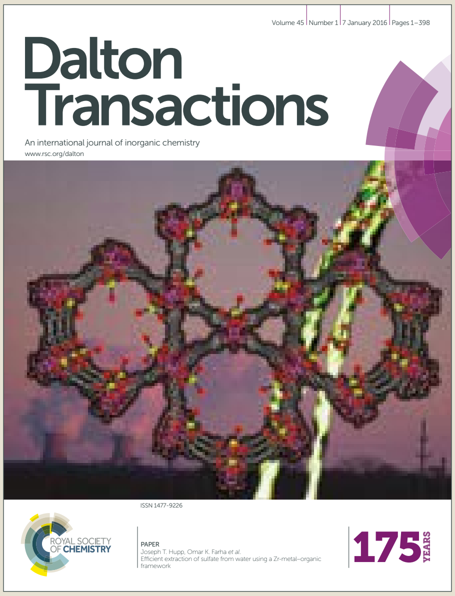

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# Exploit the Benefit of $S_0 \rightarrow T_1$ Excitation in Triplet-Triplet Annihilation Upconversion to Attain Large Anti-Stokes Shifts: Tuning the Triplet State Lifetime of a Tris(2,2'-Bipyridine) Osmium(II) Complex

Dongyi Liu, Yingjie Zhao, Zhijia Wang, Kejing Xu and Jianzhang Zhao*

Os(II) complexes are particular interesting for triplet-triplet annihilation (TTA) upconversion, due to the strong direct $S_0 \rightarrow T_1$ photoexcitation, as in this way, energy loss is minimized and large anti-Stokes shift can be achieved for TTA upconversion. However, $Os(bpy)_3$ has an intrinsic short $T_1$ state lifetime (56 ns), which is detrimental for the intermolecular triplet-triplet energy transfer (TTET), one of the crucial steps in TTA upconversion. In order to prolong the triplet state lifetime, we prepared a Os(II) tris(bpy) complex with Bodipy moiety attached, so that an extended $T_1$ state lifetime is resulted by excited state electronic configuration mixing or triplet state equilibrium between the coordination center-localized state ($^3$MLCT state) and Bodipy ligand-localized state ($^3$IL state). With steady-state and time-resolved transient absorption/emission spectroscopies, we proved that the $^3$MLCT is slightly above the $^3$IL state (by 0.05 eV), and the triplet state lifetime was prolonged by 31-fold (from 56 ns to 1.73 μs). The TTA upconversion quantum yield was increased by 4-fold as compared to that of the unsubstituted Os(II) complex.

## Introduction

Recently triplet photosensitizers have attracted much attention,[1–4] due to the applications of these versatile materials in photodynamic therapy,[2] photocatalysis such as photocatalytic hydrogen ($H_2$) production,[5–7] photoredox catalytic synthetic organic reactions,[8–13] and triplet-triplet annihilation (TTA) upconversion, etc.[14–23] TTA upconversion has attracted much attention due to its advantages over other upconversion methods, such as upconversion with two-photon absorption dyes, or rare earth materials.[24] TTA upconversion requires a triplet photosensitizer for absorbing the excitation energy and a triplet acceptor for the upconverted emission (delayed fluorescence). The energy is transferred from the photosensitizer to the acceptor molecules by intermolecular triplet-triplet-energy-transfer (TTET) process; then the excited singlet state of the acceptor will be produced and the fluorescence from the acceptor can be observed.[14–20]

Conventional triplet photosensitizers are limited to porphyrin derivatives (including Zn(II), Pt(II) or Pd(II) complexes), halogenated xanthane dyes, such as Rose Bengal or Methylene Blue, as well as some keto compounds, such as benzophenone, diacetyl, and ketocoumarin, etc.[25] Transition metal complexes such as Pt(II),[26,27] Ir(III),[28,29] Ru(II) complexes were also used as triplet photosensitizers.[30–33] However, these conventional photosensitizers suffer from drawbacks such as difficulty to prepare or purify, loss of ISC upon derivatization (although in some cases careful functionalization may leave ISC intact) or weak visible light absorption. Moreover, they share another common feature, i.e., the photoexcitation promotes the $S_0 \rightarrow S_1$ transition, then the ISC occurs and the triplet state ($T_1$ state) of the photosensitizer is populated, followed by TTET to the triplet acceptor, and TTA, finally the upconverted fluorescence is emitted.[15–16,34] Due to the large electron exchange energy ($J$) for these coplanar π-conjugated triplet photosensitizers, the energy gap between the $S_1$ state and the $T_1$ state is large ($\Delta E_{S1/T1} = 2J$), thus the energy loss from $S_1$ to $T_1$ state is large.[35] Concerning TTA upconversion, an intrinsic drawback exists with $S_0 \rightarrow S_1$ photoexcitation, i.e., the anti-Stokes shift of the upconverted emission is reduced. Larger anti-Stokes shift is desired for TTA up-conversion because photons with low energy can be converted to photons with much higher energy, for instance, red-to-blue can be resulted. However, TTA up-conversion with large anti-Stokes shifts were rarely reported.[15,16,34,36]

One method to address this drawback is to directly promote the $S_0 \rightarrow T_1$ transition by photoexcitation of the photosensitizer,

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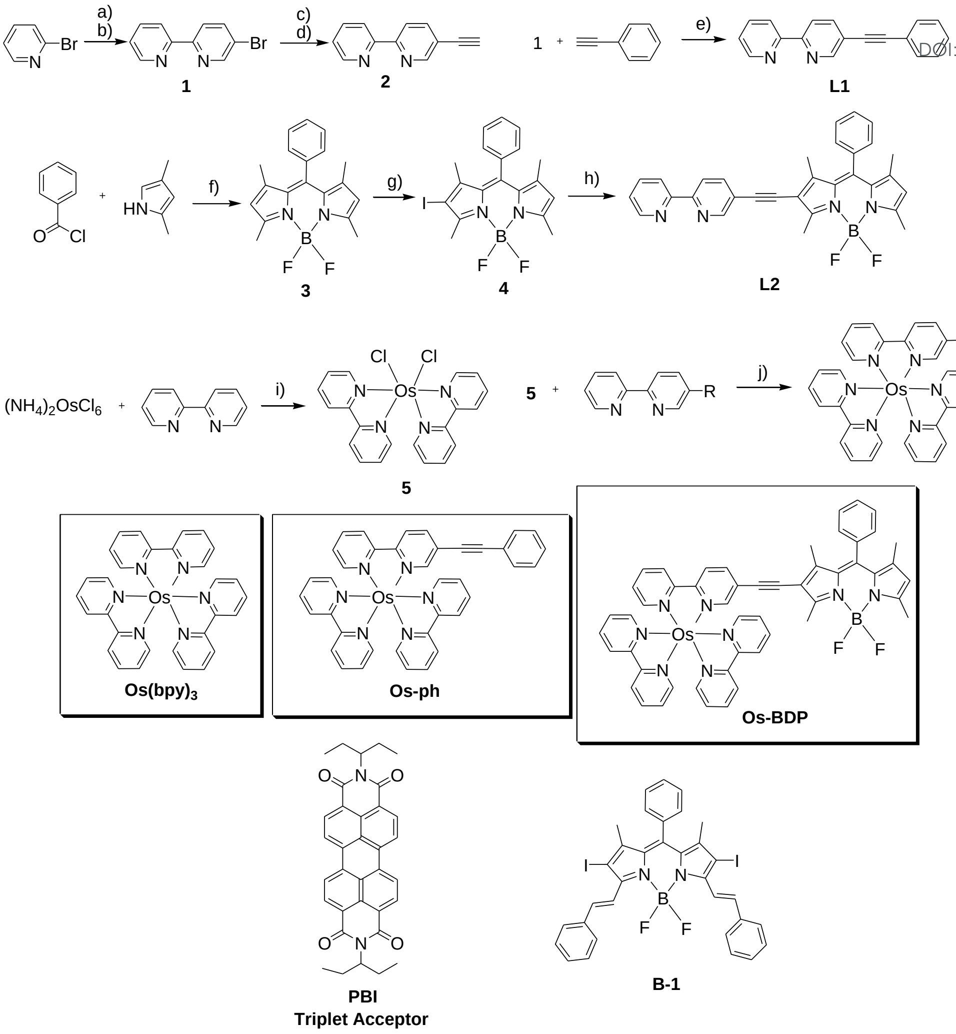

**Scheme 1**. Synthesis of the Triplet Photosensitizers **Os-BDP** and the Reference Compounds **Os(bpy)$_3$** and **Os-ph**. $^a$ Key: (a) Tributyltin chloride, diethyl ether, *n*-butyllithium, $-78$ °C to RT, $N_2$, 2 h. (b) *p*-xylene, 2,5-dibrominatedbipyridine, $Pd(PPh_3)_4$, 120 °C, $N_2$, 12 h. (c) $NEt_3$, trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, $PPh_3$, CuI, reflux, $N_2$, 8 h. (d) THF, tetrabutylammonium fluoride, RT, $N_2$, 3 h. (e) THF/ $NEt_3$, $Pd(PPh_3)_4$ , CuI, reflux, $N_2$, 14 h. (f) Dry DCM,$CF_3COOH$, RT, $N_2$, 4.5 h; DDQ, $NEt_3$, $BF_3{\cdot}NEt_3O$, ice bath, RT, $N_2$, overnight. (g) Dry DCM, NIS(1eq.), 0 °C, $N_2$, 1.5 h. (h) THF/ $NEt_3$, $PdCl_2(PPh_3)_2$, $PPh_3$, CuI, reflux, $N_2$, 8 h. (i) Ethylene glycol, reflux, $N_2$, 45 min. (j) Ethylene glycol, reflux, $N_2$, 5h.

thus the anti-Stokes shift can be increased as compared to the normal practice of $S_0 \rightarrow S_1$ excitation. Unfortunately, the photoexcitation of $S_0 \rightarrow T_1$ is a strongly forbidden transition for most chromophores, as such the molar absorption coefficient ($\varepsilon$ value) is extremely small ($< 10$ $M^{-1}$ $cm^{-1}$), which is clearly a drawback for TTA upconversion. Recently, Nobuo demonstrated that the weakly allowed $S_0 \rightarrow T_1$ transition of Os(II) complexes can be used to increase the anti-Stokes shift of TTA upconversion,[37] the anti-Stokes shift was increased to 0.86 eV. However, challenge is still present, i.e., the triplet state lifetime of the Os(II) complex in solution is very short (12 ns),[37] which is detrimental to the TTET (an intermolecular process). A longer $T_1$ state lifetime of the photosensitizer will improve the TTET efficiency, thus the TTA upconversion efficiency can be improved.

Herein, we prepared a Os(II) complex with an attached Bodipy chromophore (Scheme 1), to switch the shorter lived $^3$MLCT state of the reference Os(II) tris(bpy) complex (56 ns) to the $^3$IL state (localized on Bodipy, 1.73 μs). The photophysical properties of the Os(II) complexes were investigated by steady-state and time-resolved transient absorption/emission spectroscopies. Such an Os(II) complex containing Bodipy shows much longer triplet excited state lifetime (1.73 μs), and as a result, the TTA upconversion efficiency was improved by 4-fold. Our results are useful for the study of the photophysical properties of Os(II) complexes containing organic chromophores for electronic configuration mixing, excited state inversion, as well as for the development of new triplet photosensitizers for TTA upconversion.

## Results and Discussion

### Design and Synthesis of the Compounds

The molecular structure design of the new Os(II) complex is aimed at fully exploring the benefit of $S_0 \rightarrow T_1$ transition for TTA upconversion and to attain a triplet excited state with much

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longer lifetime. Our strategy is to attach a chromophore with proper excited state energy levels to the Os(II) coordination center, thus by transformation of the short-lived $^3$MLCT state of Os(II) complex to the ligand localized long-lived $^3$IL state, the triplet state lifetime can be prolonged.[38–43] We selected the Bodipy as chromophore, which is a versatile chromophore for its strong absorption of visible light, high quantum yield of fluorescence (repressed non-radiative decay of the excited state), and the feasible derivatization chemistry.[44–50]

Concerning our particular purpose with the Os(II) coordination center for its strong photoexcitation induced $S_0 \rightarrow T_1$ transition,[33] the Bodipy chromophore is attractive for its proper $T_1$ state energy level (1.67 eV), which matches with the $T_1$ state energy level of the **Os(II)(bpy)$_3$** coordination center (1.91 eV), thus triplet state inversion ($^3$MLCT→$^3$IL), or excited state configuration mixing can result, thus the excited state lifetime will be extended.

The synthesis of the complex **Os-BDP** is based on standard methods (Scheme 1). An ethynyl moiety was introduced on the bpy ligand, then Sonogashira coupling reaction with 2-iodo Bodipy gives the ligand **L2**. Complexation with the Os(II) precursor gives the complex **Os-BDP** with moderate yield (Scheme 1). Reference **Os-Ph** containing no Bodipy unit was also prepared (Scheme 1). All the complexes were verified with $^1$H NMR, $^{13}$C NMR and HR MS analysis (refer to Supporting Information).

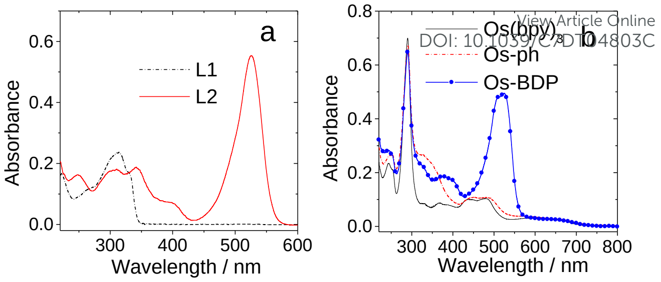

**Fig. 1** UV–Vis absorption spectra of (a) **L1** and **L2**, (b) **Os(bpy)$_3$**, **Os-ph** and **Os-BDP**. $c$ = $1.0 \times 10^{-5}$ M in $CH_3CN$, 25 °C.

## UV–Vis Absorption Spectra

The UV–Vis absorption spectra of the compounds were studied (Fig. 1). For **L1**, a moderately intense absorption band at 314 nm ($\varepsilon$ = 23300 $M^{-1}$ $cm^{-1}$) was observed. For **L2**, absorption at 342 nm ($\varepsilon$ = 18900 $M^{-1}$ $cm^{-1}$) was observed, moreover, a strong absorption band at 525 nm ($\varepsilon$ = 55400 $M^{-1}$ $cm^{-1}$) was also observed, which was the feature absorption of the Bodipy chromophore. For **Os(bpy)$_3$**, a strong absorption band at 291 nm ($\varepsilon$ = 69800 $M^{-1}$ $cm^{-1}$), a moderate absorption band at 452 nm ($\varepsilon$ = 10900 $M^{-1}$ $cm^{-1}$) and a weak absorption band at 640 nm ($\varepsilon$ = 2800 $M^{-1}$ $cm^{-1}$) were observed (Fig. 1b); for **Os-Ph**, similar absorption bands were also observed (Fig. 1b), these absorption bands were the feature absorptions of the Os(II) coordination center, the weak and broad absorption band at 500–700 nm is due to the $S_0 \rightarrow T_1$ transition. For **Os-BDP**, strong

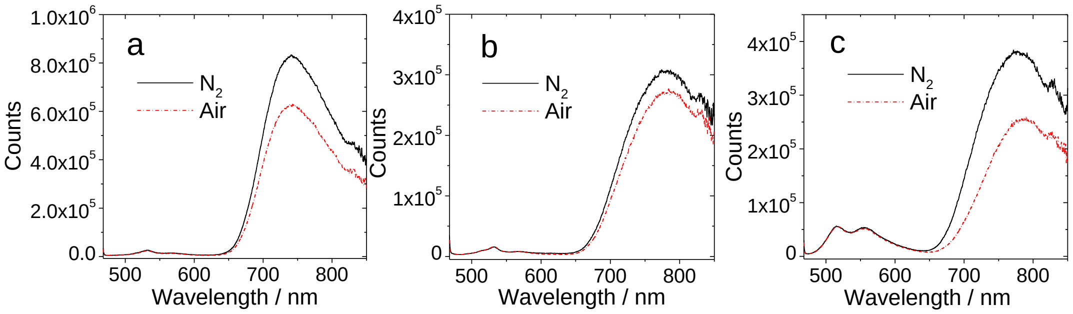

**Fig. 2** Luminescence emission spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP**; $\lambda_{ex}$ = 460 nm, $c$ = $1.0 \times 10^{-5}$ M in $CH_3CN$, 25 °C.

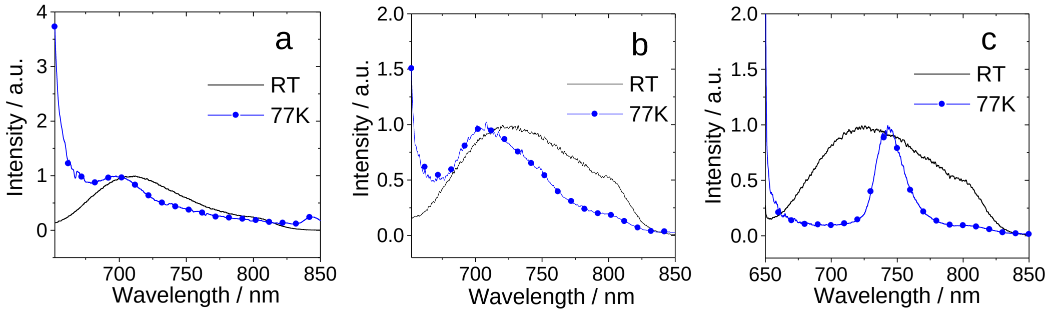

**Fig. 3** Luminescence emission spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP** at RT compared with those at 77 K, $\lambda_{ex}$ = 635 nm, $c$ = $1.0 \times 10^{-5}$ M in aerated EtOH/MeOH mixed solvent (4:1, v/v), under $N_2$.

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**Table 1.** Photophysical Properties of the Compounds

| Complexes | $\lambda_{\mathrm{abs}}$ [a] (nm) | $\varepsilon$ [b] ($10^4$ $M^{-1}cm^{-1}$) | $\lambda_{\mathrm{em}}$ [c] (nm) | $\Phi_{\Delta}$ [d] | $\Phi_{\mathrm{L}}$ (%) [e] | $\tau_{\mathrm{L}}$ (ns) [f] [298 K] | $\tau_{\mathrm{L}}$ (μs) [f] [77 K] | $\tau_{\mathrm{T}}$ (ns) [g] [$N_2$] | $\tau_{\mathrm{T}}$ (ns) [g] [Air] |
|---|---|---|---|---|---|---|---|---|---|
| **Os(bpy)₃** | 291/452/640 | 6.98/1.09/0.28 | 740 | 0.85 | 1.19 | 54 | 0.869 | 56 | 46 |
| **Os-ph** | 291/435/636 | 6.75/1.0/0.3 | 779 | 0.31 | 0.53 | 46 | 0.797 | 23 | 21 |
| **Os-BDP** | 290/525/650 | 6.48/4.95/0.25 | 515/565/778 | 0.64 | 0.39 | 53 (95%)<br>732(5%) | 12.37(99.25%)<br>205.29(0.75%) | 1729 | 255 |
| **L1** | 314 | 2.33 | –[h] | –[h] | –[h] | 0.72 | –[h] | –[h] | –[h] |
| **L2** | 342/525 | 1.89/5.54 | 565 | –[h] | –[h] | 3.8 | –[h] | –[h] | –[h] |

[a] Maximum UV–Vis absorption wavelengths in $CH_3CN$, $c = 1.0 \times 10^{-5}$ M, 25 °C. [b] Molar absorption coefficient at absorption maxima. [c] Maxima emission wavelengths in $CH_3CN$, $\lambda_{\mathrm{ex}} = 460$ nm, $c = 1.0 \times 10^{-5}$ M, 25 °C. [d] Singlet oxygen quantum yields ($\Phi_{\Delta}$) with Rose Bengal as a standard ($\Phi_{\Delta} = 0.8$ in MeOH), in $CH_3CN$, **Os(bpy)₃** ($\lambda_{\mathrm{ex}} = 496$ nm), **Os-ph** ($\lambda_{\mathrm{ex}} = 497$ nm), **Os-BDP** ($\lambda_{\mathrm{ex}} = 545$ nm), 25 °C. [e] Luminescence quantum yields ($\Phi_{\mathrm{L}}$) with 2,6-diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene as a standard ($\Phi_{\mathrm{L}} = 2.7\%$ in $CH_3CN$)[60], in $CH_3CN$, $\lambda_{\mathrm{ex}} = 400$ nm, 25 °C. [f] Luminescence lifetimes in EtOH/MeOH (4:1, v/v, $c = 1.0 \times 10^{-5}$ M), under $N_2$, 20 °C. [g] Triplet state lifetimes of the complexes were measured by nanosecond transient absorption (collinear mode) in $CH_3CN$, **Os(bpy)₃** ($\lambda_{\mathrm{ex}} = 472$ nm, c = $5.0 \times 10^{-6}$ M), **Os-ph** ($\lambda_{\mathrm{ex}} = 442$ nm, $c = 1.0 \times 10^{-5}$ M), **Os-BDP** ($\lambda_{\mathrm{ex}} = 502$ nm, $c = 2.5 \times 10^{-6}$ M), 20 °C. [h] Not applicable.

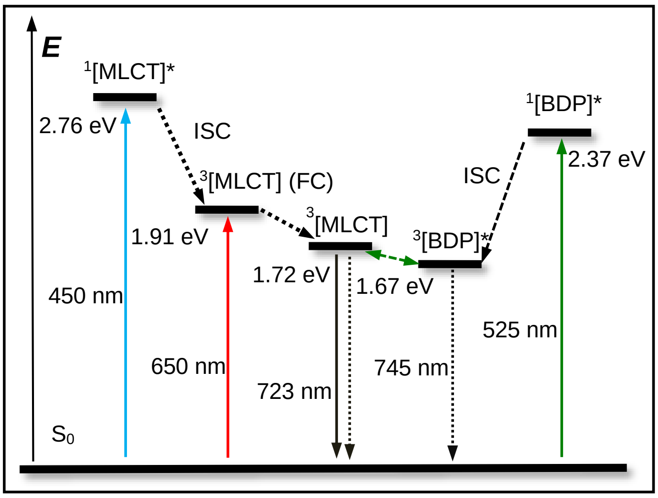
absorption at 290 nm ($\varepsilon = 64800$ $M^{-1}$ $cm^{-1}$) and weak absorption at 650 nm ($\varepsilon$ = 2500 $M^{-1}$ $cm^{-1}$) were observed, these two absorption bands were the feature absorption of the Os moiety, meanwhile, a strong absorption band at 525 nm ($\varepsilon = 49500$ $M^{-1}$ $cm^{-1}$) was observed, which is the feature absorption of the Bodipy chromophore. The absorption spectrum of **Os-BDP** is not the sum of **L2** and **Os(bpy)₃** concerning the molar absorption coefficients, although the absorption wavelengths are similar. It may be due to the π-conjugation between the Os(II) coordination center and the Bodipy chromophore. The UV-Vis absorption of the compounds in other solvents were also studied (see ESI†, Fig. S11).

### Luminescence Emission Spectra

The emission properties of the complexes were studied under different atmospheres (Fig. 2). For **Os(bpy)₃** (Fig. 2a), a broad emission band at 650–850 nm ($\lambda_{\mathrm{max}}$ = 740 nm) was observed. The luminescence intensity of the structureless emission band can be quenched by 25 % in air as compared to the aerated solution. For **Os-ph** (Fig. 2b), a broad emission band at 650–850 nm ($\lambda_{\mathrm{max}}$ = 779 nm) was observed, the intensity of the structureless emission band can be quenched by 11 % in air as compared to the aerated solution. These results indicate that the excited state lifetime is short, otherwise the quenching of the phosphorescence will be more significant. For **Os-BDP** (Fig. 2c), the luminescence intensity of the structureless emission band at 650–850 nm ( $\lambda_{\mathrm{max}}$ = 778 nm) can be quenched by 33% in air as compared to the aerated solution, however, the luminescence intensity of a weak emission band at 500–650 nm has no difference in air as compared to the deaerated solution. The $O_2$ sensitivity of the emission bands indicates that the emission of **Os-BDP** at 500–650 nm is due to the fluorescence of Bodipy moiety, the emission band at 650–850 nm is the phosphorescence, based on the drastically different Stokes shift and the luminescence lifetimes.

The luminescence spectra of the complexes at RT were compared with those at 77 K (Fig. 3). For **Os(bpy)₃** and **Os-ph**, the emission bands are blue-shifted by 0.02 eV at 77 K as compared to those at RT. This result is reasonable since the emissive triplet excited states of **Os(bpy)₃** and **Os-ph** are $^3$MLCT states, which are known to show blue-shifted emission in frozen solution (for instances, at 77 K). This blue-shiftted emission in frozen matrix is due to the inability of the solvent shell to re-adjust in the solid matrix, $^3$MLCT state is in charge transfer feature, as a result the $^3$MLCT state is less stabilized by solvation, as a result, the emission is blue-shifted in the solid matrix.

For **Os-BDP**, interestingly, a narrower emission band was observed at 745 nm (Fig. 3c), at 77 K. This emission band is assigned as the $^3$IL state localized on the Bodipy entity of the substituted bipy ligand. Previously similar phosphor-rescence band of Bodipy ligand in transition metal complexes at low temperature was reported at 740 nm.[52] Based on the result, we propose that in RT fluid solution, the $^3$MLCT state energy level is higher than the $^3$IL state ($\Delta E \approx 0.05$ eV). This energy gap is significantly larger than the thermal energy at 77 K (0.007 eV), thus there is no state mixing at 77 K for **Os-BDP**. In other words, at 77 K, due to the decreased thermal energy, as well as the higher energy of the $^3$MLCT (matrix effect), the $^3$IL state is sufficiently lower than the $^3$MLCT state, as a result, the emission



**Scheme 2.** Qualitative Jablonski Diagram for the Photophysical Process of the Os(II) Complexes Exemplified with **Os-BDP**. Solid lines represent excitation or radiative processes; dotted lines represent non-radiative processes. Note the $^3$MLCT phosphorescence is quenched by the low-lying $^3$Bodipy* state. IC: internal conversion, ISC: intersystem crossing, FC: Franck-Condon.

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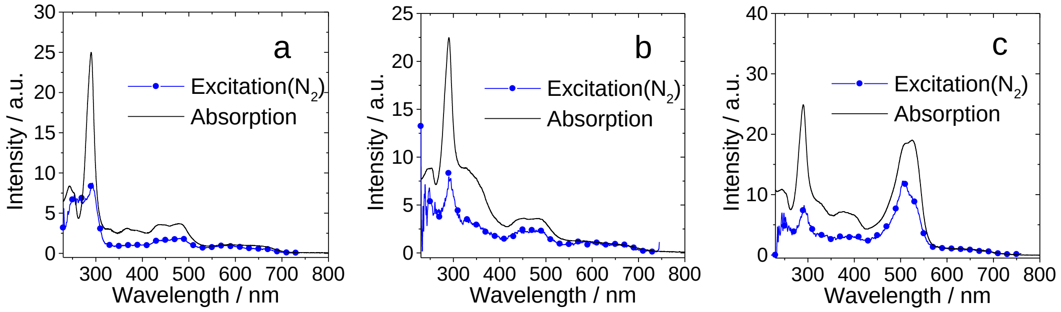

**Fig. 4** The normalized UV–Vis absorption and the excitation spectra of (a) **Os(bpy)$_3$**, (b) **Os-ph**, (c) **Os-BDP**. The excitation spectra of Os(Ⅱ) complexes were recorded with $\lambda_{em1}$ = 745 nm (**Os(bpy)$_3$**), $\lambda_{em2}$ = 750 nm (**Os-ph**) and $\lambda_{em3}$ = 765 nm (**Os-BDP**). $c$ = 1.0 × $10^{-5}$ M in $CH_3CN$, 25 °C.

of **Os-BDP** at 77 K is due to $^3$IL state, which is different from that of **Os(bpy)$_3$** and **Os-Ph**. According to these information, the photophysical processes of the Os(II) compl-exes exemplified with **Os-BDP** are shown in Scheme 2.

### Comparison of the luminescence excitation spectra and the normalized UV–Vis absorption spectra

In order to study the intramolecular energy transfer in **Os-BDP**, the luminescence excitation spectra of the complexes were recorded and compared with the normalized UV–Vis absorption spectra (Fig. 4).

The normalized UV–Vis absorption spectroscopies and the photo-luminescence excitation spectroscopies cannot be completely overlapped in the higher energy region, given the spectra are normalized to the $S_0 \rightarrow T_1$ absorption band. This result indicates that the decay of the higher excited $S_n$ state to $S_1$ state (or intersystem crossing to the emissive $T_1$ state) has no unitarian yield (there are most like more than one higher excited states involved), and there are other non-radiative decay channels. For **Os-BDP** (Fig. 4c), the emission wavelength was set at 765 nm, we found that the absorption of the Bodipy part at 525 nm is effective to produce the near IR emission at 765 nm. This result indicates efficient energy transfer from the Bodipy moiety to the Os(II) coordination center, by a singlet energy transfer, or a triplet energy transfer.[53] The three complexes show similar emission bands at similar wavelengths, thus all the luminescence were assigned as the $T_1 \rightarrow S_0$ phosphorescence of the Os(II) coordination center. Previously the phosphorescence of Bodipy was reported as a narrow, structured emission band at 730 nm,[51] although the phosphorescence emission wavelength of Bodipy was close to the phosphorescence of the Os(II) coordination center. The luminescence of **L2** and **Os-BDP** were compared for optically matched solutions (see ESI†, Fig. S3a). The fluorescence of **L2** is drastically quenched in **Os-BDP**, most likely by the heavy atom effect of Os, i.e. ISC effect. It was also found that the phosphorescence of **Os-ph** and **Os-BDP** were decreased as compared to **Os(bpy)$_3$** (see ESI†, Fig. S13b). The luminescence quantum yields of the complexes were also studied (Table 1), **Os(bpy)$_3$** ($\Phi_L$ = 1.19%), **Os-ph** ($\Phi_L$ = 0.53%) and **Os-BDP** ($\Phi_L$ = 0.39%), and the luminescence quantum yields of **Os-ph** and **Os-BDP** were decreased as compared to **Os(bpy)$_3$**.

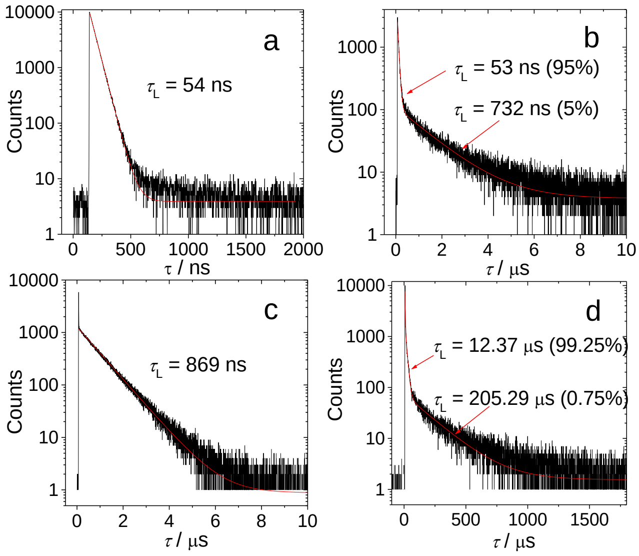

**Fig. 5** Luminescence lifetimes decay trace of (a) **Os(bpy)$_3$** ($\lambda_{em}$ = 715 nm) and (b) **Os-BDP** ($\lambda_{em}$ = 730 nm) at RT; (c) **Os(bpy)$_3$** ($\lambda_{em}$ = 705 nm) and (d) **Os-BDP** ($\lambda_{em}$ = 745 nm) at 77 K, $\lambda_{ex}$ = 635 nm, c = 1.0 × $10^{-5}$ M in aerated EtOH/MeOH (4:1, v/v).

### Luminescence lifetimes at room temperature and 77 K

The phosphorescence lifetimes of the complexes were measured with the TCSPC (Fig. 5). Although the three complexes give similar emission band, the phosphorescence lifetime of **Os-BDP** (732 ns, the long-lived component of the biexponential decay) is drastically different from that of **Os(bpy)$_3$** (54 ns) and **Os-ph** (46 ns). This result indicates that the emissive $^3$MLCT state of **Os-BDP** is significantly perturbed by another state, or electronic configuration mixing, most pro-bably by the $^3$IL state localized on the Bodipy ligand. The comparison of the phosphorescence of **Os-BDP** at room temperature and 77 K indicates that the $^3$MLCT state lies above

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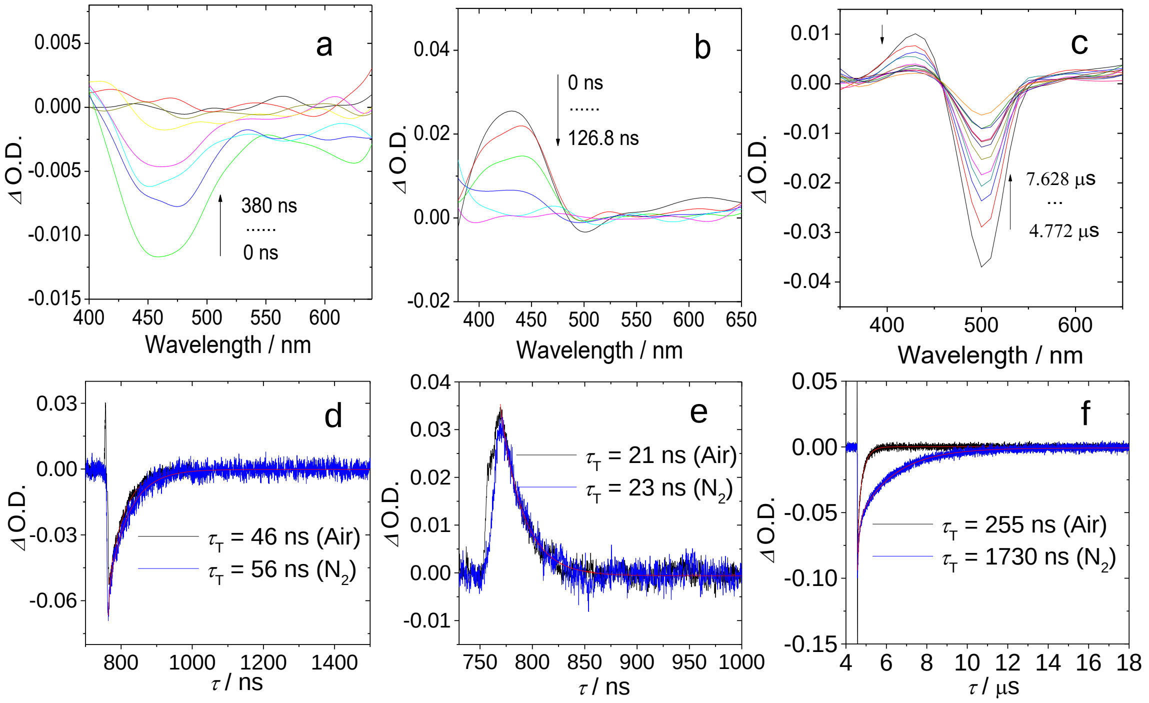

**Fig. 6** Transient absorption spectra of (a) **Os(bpy)$_3$**, $\lambda_{ex}$ = 480 nm, $c$ = 3.0 × 10$^{-5}$ M; (b) **Os-ph,** $\lambda_{ex}$ = 480 nm, $c$ = 5.0 × 10$^{-5}$ M; (c) **Os-BDP**, $\lambda_{ex}$ = 502 nm, $c$ = 2.5 × 10$^{-6}$ M in aerated and deaerated $CH_3CN$. Triplet lifetime decay trace of (d) **Os(bpy)$_3$**, $\lambda_{ex}$ = 472 nm, $c$ = 5.0 × 10$^{-6}$ M; (e) **Os-ph**, $\lambda_{ex}$ = 442 nm, $c$ = 1.0 × 10$^{-5}$ M; (f) **Os-BDP**, $\lambda_{ex}$ = 502 nm, $c$ = 2.5 × 10$^{-6}$ M in $CH_3CN$, 25 °C.

the $^3$IL state by only 0.05 eV (Fig. 3 and Scheme 2). The luminescence lifetimes of the complexes at 77 K were also determined (Fig. 5). The lifetimes of **Os(bpy)$_3$** and **Os-ph** were extended by ca. 17-fold by decreasing the temperature from RT to 77 K, indicating the emissive triplet states are similar for both complexes. For **Os-BDP** (Fig. 5b and Fig. 5d), however, the phosphorescence lifetimes increased by ca. 233-fold/280-fold by decreasing the temperature, which extended from 0.05 μs/0.732 μs (RT) to 12.37 μs/205.29 μs (77 K). It should be noted that the 12.73 μs is the slow limit because it is the instrument response function (IRF). This result indicates that the property of the emissive triplet state changed significantly by changing the temperature and it is in agreement with the postulates that the emissive state of **Os-BDP** at RT is $^3$MLCT, but inversion of the triplet state energy levels ($^3$MLCT vs. $^3$IL states) occurs at 77 K, and it is the $^3$IL state at 77 K. Long-lived triplet excited state of Bodipy were observed with Ir(III) complexes at 77 K (4.5 ms),[51,54] as well as Ru(II) complexes (339 ms).[52] The significantly shorter triplet state lifetime in **Os-BDP** as compared to that of the Ir(III) and Ru(II) complexes may be due the more significant heavy atom effect of Os atoms than Ir and Ru atoms.[33,55–57] The biexponential character of the decay curves of **Os-BDP** were observed at RT and 77 K, but the exact reason for these biexponential decay is unclear.

To verify the efficiency of the triplet state yields of the triplet photosensitizers **Os(bpy)$_3$**, **Os-ph** and **Os-BDP**, the singlet oxygen ($^1O_2$) quantum yields ($\Phi_\Delta$) of the triplet photosensitizers were studied. With selective photoexcitation at the energy donor absorbance, $\Phi_\Delta$ values of 85%, 31% and 64% were observed for **Os(bpy)$_3$**, **Os-ph** and **Os-BDP** in $CH_3CN$, respectively (Table 1).

### Nanosecond Transient Absorption Spectroscopy

In order to investigate the triplet excited state of the complexes, the nanosecond transient absorption (ns TA) spectroscopies of **Os(bpy)$_3$**, **Os-Ph** and **Os-BDP** are studied(Fig. 6), and triplet lifetimes were presented in Table 1.

Upon 472 nm pulsed laser photoexcitation, a weak bleaching band at 460 nm was observed for **Os(bpy)$_3$** (Fig. 6a). The lifetime of **Os(bpy)$_3$** was very short, it was determined as 56 ns (under $N_2$ atmosphere), and a weak positive absorption band at 430 nm was observed for **Os-ph** (Fig. 6b), the lifetime of **Os-ph** was also very short, it was determined as 23 ns (in $N_2$ saturated solution).

Upon 502 nm pulsed laser photoexcitation, a bleaching band at 503 nm was observed for **Os-BDP** (Fig. 6c). This band overlaps with the transient absorption band in the range of 450 nm–555 nm. The excited state absorption (ESA) profile is the typical $T_1 \rightarrow T_n$ absorption of the Bodipy triplet excited state. Thus, the detected triplet excited state of **Os-BDP** is localized on the Bodipy ligand. However, the triplet state localization on the Os(II) coordination center cannot be excluded. The lifetime of **Os-BDP** was determined as 1.73 μs ($N_2$, excited at 502 nm), which is much longer than **Os(bpy)$_3$** (56 ns).

Interestingly, we found that the triplet state lifetime is not excitation wavelength-dependent (see ESI†, Fig. S19). For instance, selective excitation either into the Bodipy moiety

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(excited at 502 nm) or the Os(II) coordination center (excited at 650 nm), gives very similar triplet state lifetimes of 1.73 μs vs 1.21 μs (see ESI†, Fig. S19), respectively. This result indicates a fast intra-molecular energy transfer.

Based on the lifetimes, we estimated the equilibrium constant of the $^3$MLCT/$^3$IL state in **Os-BDP**.[58]

$$\frac{1}{\tau} = \alpha\frac{1}{\tau_{\mathrm{BDP}}} + (1-\alpha)\frac{1}{\tau_{\mathrm{MLCT}}} \qquad (1)$$

$$\frac{\alpha}{1-\alpha} = k_{\mathrm{eq}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} \qquad (2)$$

$\alpha$ corresponds to the fractions of the excited BDP-like triplets, $\tau$ is the lifetime decay of metal complexes, where $\tau_{\mathrm{MLCT}}$ and $\tau_{\mathrm{BDP}}$ correspond to the time constants for the decays of the excited **Os(II)(bpy)$_3$** coordination center and BDP ligand. $k_{\mathrm{eq}}$ is the equilibrium constant and $k_{\mathrm{f}}$ is the forward energy transfer and $k_{\mathrm{b}}$ is the backward energy transfer rate constant. For the system at room temperature, we approximate the $\tau_{\mathrm{BDP}}$ as 100 μs and $\tau_{\mathrm{MLCT}}$ as 60 ns, then based on eq. (1) and (2), $\alpha$ was calculated as 0.96, the $k_{\mathrm{eq}}$ = 24. This result means that the equilibrium population is predominantly (96%) in favor of the BDP chromophore ($^3$IL state), not the Os(II) coordination center ($^3$MLCT state). Similarly, we estimated the equilibrium at 77 K with eq. (1) and (2), with approximation of $\tau_{\mathrm{BDP}}$ =10 ms (77 K) and $\tau_{\mathrm{MLCT}}$ = 800 ns (77 K). The $k_{\mathrm{eq}}$ was calculated as 250. Thus at 77 K, the triplet state is basically a $^3$IL state. This conclusion is in agreement with the spectroscopic studies, for instance the observation of the BDP-localized signal in the nanosecond transient absorption spectroscopy. However, the $^3$MLCT lies only slightly higher than $^3$IL state (by 0.05 eV), thus the decay of the $^3$IL state is fast via the drain channel, i.e., the short-lived $^3$MLCT state of the Os(II) coordination center.

### Triplet-Triplet Annihilation Upconversion

Since we extended the triplet state lifetimes of the Os(II) complexes, the complexes described herein were used as triplet photosensitizers for another triplet-triplet energy transfer (TTET) process, i.e., TTA upconversion (Fig. 7). A 635 nm cw-laser was used as excitation source. Based on the T$_1$ state energy levels, we used **PBI** as triplet acceptor/emitter ($E_{\mathrm{T1}}$ = 1.2 eV, Scheme 1). For the photo-sensitizers alone, no emission in the range of 550 nm was observed (Fig. 7a). In the presence of **Os-BDP**, however, significant upconverted emission at 550 nm was observed (Fig. 7b), which is much stronger than that of **Os(bpy)$_3$** or **Os-Ph**. The upconversion quantum yield with **Os-BDP** (1.2%) is much higher than that of the **Os(bpy)$_3$** (0.3%) or **Os-ph** (0.17%). It should be noted that the triplet state lifetimes of the three Os(II) complexes play a major role for the variation of the upconversion quantum yields. In order to study the TTET efficiency of TTA upconversion, quenching the luminescence lifetime of the Os(II) complexes by triplet acceptor **PBI** was studied (Fig. 8). The $K_{\mathrm{SV}}$ value of **Os-BDP** is ca. 5-fold for **Os(bpy)$_3$**, ca. 3.5-fold for **Os-ph** (Table 2).

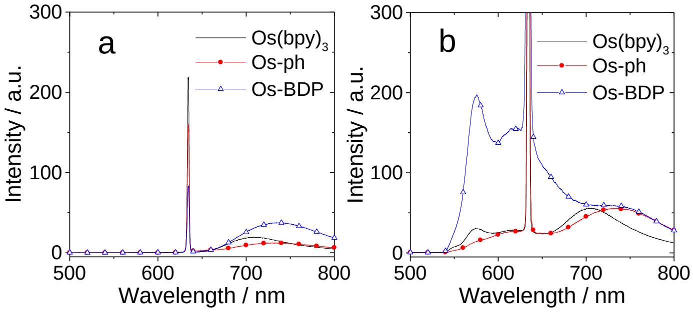

**Fig. 7** Upconversion with **Os(bpy)$_3$**, **Os-ph** and **Os-BDP** as triplet photosensitizers and PBI as triplet acceptor, excited by a 635 nm laser (continuous wave, 300 mW cm$^{-2}$). (a) Emission of the complexes alone with a 635 nm laser excitation. (b) Upconversion emission of the mixtures of the photosensitizers and PBI upon selective excitation of photosensitizers with a 635 nm laser. $c$[Photosensitizers] = 1.0 × 10$^{-4}$ M and $c$[**PBI**] = 2.5 × 10$^{-3}$ M. In deaerated DCM, 25 °C.

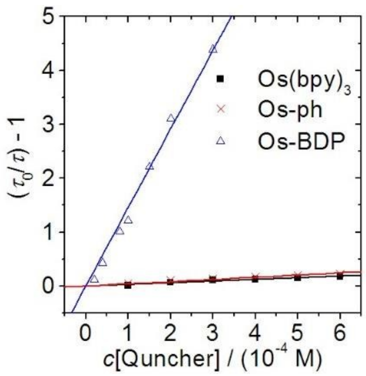

**Fig. 8** Stern-Volmer plots generated from luminescence lifetime ($\tau_{\mathrm{L}}$) quenching of **Os(bpy)$_3$**, **Os-ph** and **Os-BDP** measured as a function of the concentration of quencher (PBI). Luminescence lifetimes ($\tau_{\mathrm{L}}$) were measured by excitation at $\lambda_{\mathrm{ex}}$ = 635 nm, $c$[photosensitizers] = 1.0 × 10$^{-4}$ M in deaerated dichloromethane, 20 °C.

**Table 2.** Upconversion-Related Parameters of the Os(II) Complexes

| Sensitizers | $\Phi_{\mathrm{UC}}$ (%) [a] | $K_{\mathrm{sv}}$ (M$^{-1}$) [b] | $\tau_{\mathrm{L}}$ (ns) [c] | $k_{\mathrm{q}}$ (10$^9$M$^{-1}$ s$^{-1}$) [d] |
|---|---|---|---|---|
| **Os(bpy)$_3$** | 0.30 | 303.7 | 88.5 | 3.43 |
| **Os-ph** | 0.17 | 411.1 | 71.6 | 5.74 |
| **Os-BDP** | 1.20 | 14568.0 | 1301.7 | 11.2 |

[a] Upconversion quantum yields were measured with **B-1** as the standard ($\Phi_{\mathrm{F}}$ = 0.101 in DCM), $\lambda_{\mathrm{ex}}$ = 635 nm, $c$[Photosensitizers] = 1.0 × 10$^{-4}$ M and $c$[**PBI**] = 2.5 × 10$^{-3}$ M. In aerated DCM, 20 °C. [b] Stern-Volmer quenching constants ($K_{\mathrm{sv}}$) for the luminescence lifetime of Os(II) complexes, quenched by **PBI**. [c] Luminescence lifetimes of **Os(bpy)$_3$**, **Os-ph** and **Os-BDP**, $\lambda_{\mathrm{ex}}$ = 635 nm, $c$[photosensitizers]= 1.0 × 10$^{-4}$ M in aerated dichloromethane, 20 °C. [d] Bimolecular quenching constants ($k_{\mathrm{q}}$), $K_{\mathrm{sv}} = k_{\mathrm{q}}\tau_0$, $\tau_0$ is the luminescence lifetime of photosensitizers without quencher.

## Conclusions

In summary, in order to fully exploit the benefit of direct S$_0$→T$_1$ photoexcitation of the **Os(bpy)$_3$** complex (bpy = 2,2'-bipyridine)

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to reduce the energy loss for the $S_1 \rightarrow T_1$ intersystem crossing of the normal triplet photosensitizers, the intrinsic short $T_1$ state lifetime (56 ns) of **Os(bpy)$_3$** has to be prolonged, otherwise the intermolecular triplet-triplet-energy-transfer efficiency is low. To this end, a Bodipy moiety was attached to the bpy ligand of the **Os(bpy)$_3$** coordination framework, to establish an excited states equilibrium to extend the triplet lifetimes. With steady-state and time-resolved transient absorption spectroscopies, we proved the energy transfer from Bodipy moiety to the Os(II) coordination center. Based on the phosphorescence emission wavelength at room temperature and 77 K, we propose the $^3$MLCT state lies slightly higher than the Bodipy localized $^3$IL state by 0.05 eV. With this molecular structure design and thus the $T_1$ state lifetime was extended from the 56 ns of the un-substituted Os(II) complex to 1.73 μs. With the Os(II) complex containing Bodipy moiety, triplet-triplet annihilation quantum yield was increased to 1.2 %, as compared to 0.3 % of the reference Os(II) complex. The anti-Stokes shift is 0.55 eV. Our results are useful for exploitation the novel $S_0 \rightarrow T_1$ photoexcitation, as well as for achieving large anti-Stokes shift for TTA upconversion.

## Experimental Section

### Analytical Measurements

All the chemicals used in synthesis are analytically pure and were used as received. Solvents were dried and distilled before used for synthesis. The synthesis of compounds **1-5** and **L2** were reported elsewhere.[52,59]

**Synthesis of Os(bpy)$_3$**. Under $N_2$, 2,2'-bipyridine (8.0 mg, 0.05 mmol) and **5** (29 mg, 0.05 mmol) were added to ethylene glycol (8 mL), bubbled with $N_2$ for 20 min and refluxed for 5 h. The mixture was cooled to room temperature, the solvent was removed under reduced pressure. Then saturated $NH_4PF_6$ solution was added dropwise, and the suspension was stirred for 15 min and then filtered to remove insoluble inorganic salts. The solution was evaporated to dryness under reduced pressure to obtain a dark-green solid. The crude product was further purified by column chromatography (aluminium oxide, DCM:MeOH, 100:0 to 90:10, v/v) to afford a dark-green solid (28.0 mg, 58.3%). $^1$H NMR (500 MHz, d$_6$-DMSO) $\delta$ 8.83 (d, $J$ = 8.2 Hz, 1H),7.97 (dd, $J$ = 11.6, 4.2 Hz, 1H), 7.66 (t, $J$ = 13.4 Hz, 1H), 7.43 (t, $J$ = 6.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 211.79, 164.26, 156.24, 156.04, 143.23, 142.46, 133.42, 133.28, 129.87, 129.71, 122.61, 73.08, 43.98, 35.49, 35.20, 34.01, 28.90, 27.99, 18.64, 15.66, 6.11, 5.94, 5.78, 5.61, 5.53, 5.45, 5.37, 5.28, 5.21, 5.12. ESI-HRMS: [$(M-2PF_6)^{2+}$] cal., $m/z$ = 330.0839, found, $m/z$ = 330.0859; [$(M-PF_6)^+$] cal., $m/z$ = 805.1319, found, $m/z$ = 805.1323.

**Synthesis of Os-ph**. Under $N_2$, **L1** (26 mg, 0.1 mmol) and **5** (57 mg, 0.1 mmol) were added to ethylene glycol (10 mL), bubbled with $N_2$ for 20 min and refluxed for 7 h. The mixture was cooled to room temperature. The crude product was purified with column chromatography ($CH_3CN$:$H_2O$:$KNO_3$ (saturated water solution) = 100:10:1, v/v/v). The solvent was removed under reduced pressure, a small amount of $CH_3CN$:$H_2O$ = 1:1 (v/v) mixture was added to dissolve the solid completely, then saturated $NH_4PF_6$ solution was added dropwise. The suspension was filtered to remove insoluble inorganic salts and the solid was washed with water. A dark-green solid (50 mg, 47.6%) was afforded. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.58–8.44 (m, 6H), 7.99–7.81 (m, 6H), 7.75 (d, $J$ = 5.8 Hz, 1H), 7.64 (dd, $J$ = 17.1, 8.3 Hz, 5H), 7.47 (ddd, $J$ = 22.9, 16.2, 7.7 Hz, 4H), 7.38–7.26 (m, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 164.27, 164.15, 163.76, 163.69, 157.82, 157.64, 156.63, 156.41, 156.36, 156.15, 156.08, 155.87, 144.30, 143.17, 142.58, 141.29, 139.96, 137.11, 136.92, 135.34, 134.17, 133.38, 132.32, 130.67, 130.38, 129.90, 129.74, 129.48, 129.25, 127.53, 126.54, 122.64, 114.19, 101.80, 88.93, 70.01, 69.98, 48.03, 6.11, 5.95, 5.78, 5.62, 5.45, 5.37, 5.29, 5.21, 5.12. ESI-HRMS: [$(M-2PF_6)^{2+}$] cal., $m/z$ =380.0995, found, $m/z$ = 380.0999; [$(M-PF_6)^+$] cal., $m/z$ = 905.1632, found, $m/z$ = 905.1653.

**Synthesis of Os-BDP**. Under $N_2$, **L2** (21 mg, 0.042 mmol) and **5** (26 mg, 0.045 mmol) were added to ethylene glycol (5 mL), bubbled with $N_2$ for 20 min and refluxed for 4 h. The mixture was cooled to room temperature. The crude product was purified with column chromatography ($CH_3CN$:$H_2O$:$KNO_3$ (saturated water solution) = 100:10:1, v/v/v). The solvent was removed under reduced pressure, a small amount of $CH_3CN$:$H_2O$ = 1:1 (v/v) mixture was added to dissolve the solid completely, then, saturated $NH_4PF_6$ solution was added drop-wise. The suspension was filtered to remove insoluble inorganic salts and the solid was washed with water. A dark-red solid (15 mg, 27.6%) was afforded. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.54–8.40 (m, 6H), 7.94–7.80 (m, 6H), 7.73 (d, $J$ = 5.3 Hz, 1H), 7.68–7.54 (m, 8H), 7.39–7.28 (m, 7H), 6.26 (s, 1H), 2.56 (s, 3H), 2.52 (s, 3H), 1.45 (d, $J$ = 3.7 Hz, 3H), 1.39 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 158.59, 158.54, 158.50, 158.16, 157.21, 151.51, 150.88, 150.75, 150.62, 150.58, 150.46, 137.31, 137.00, 136.96, 136.93, 136.87, 136.82, 133.64, 129.15, 129.09, 127.79, 127.74, 127.70, 127.66, 127.57, 124.55, 124.38, 124.33, 124.19, 124.16, 123.70, 123.02, 116.99, 90.27, 90.22, 54.01, 26.35, 26.31, 13.81, 13.59, 12.26, 11.92. ESI-HRMS: [$(M-2PF_6)^{2+}$] cal., $m/z$ = 503.1565, found, $m/z$ =503.1566; [$(M-PF_6)^+$] cal., $m/z$ = 1151.2772, found, $m/z$ = 1151.2786.

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# Table of Contents Entry

## Exploit the Benefit of $S_0 \rightarrow T_1$ Excitation in Triplet-Triplet Annihilation Upconversion to Attain Large Anti-Stokes Shifts: Tuning the Triplet State Lifetime of a Tris(2,2'-Bipyridine) Osmium(II) Complex

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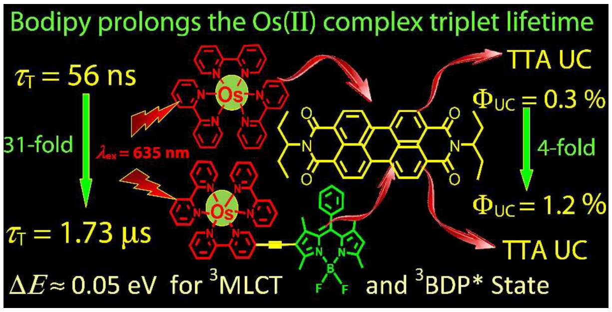

The triplet state lifetime of $Os(bpy)_3$ complex showing strong $S_0 \rightarrow T_1$ absorption was prolonged 30-fold by attachment of Bodipy Chromophore.