Switchable Ambient-Temperature Singlet–Triplet Dual Emission in Nonconjugated Donor–Acceptor Triarylboron–Pt^{II} Complexes

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Abstract: A triarylboron compound Si-BNPA (1) containing a BMes₂ acceptor and an N-(2'-pyridyl)-7-azaindolyl (NPA) donor linked by a tetrahedral silane group has been synthesised. This molecule displays unusual white singlet-triplet dual emission at 77 K, with an exceptionally long phosphorescent decay time (2.2 s). Fluoride titration experiments established that the singlet and triplet emission peaks are due to acceptor-based Mes→B charge transfer and donor-based ${}^{3}\pi \rightarrow \pi^{*}$ transitions, respectively. This dual emission was found to be persistent and observable at ambient temperature in its PtII complex [Pt(N,N-Si-BNPA)Ph₂] (2a). Furthermore, 2a was found to undergo intramolecular "roll-over" C-H activation to produce the N,C-chelate complex [Pt(N,C-Si-BNPA)(SMe₂)Ph] (**2b**). This compound also displays ambient temperature singlet-triplet dual emission, but with a much greater phosphorescent efficiency than **2a** due to the formation of a more stable chelate ring. Addition of fluoride was found to have little impact on the phosphorescent emission of **2a**, but resulted in a large enhancement of the phosphorescent emission intensity of **2b**. To establish the impact of donor-acceptor geometry on this singlet-triplet dual emission, the properties of linearly conjugated donor-acceptor complexes [Pt-

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 $(N,N-BNPA)Ph_2$] (3a) and [Pt(N,C- $BNPA)Ph_2$ (3b) were also examined. Consistent with 2a and 2b, the N,Cchelate complex 3b has a much higher phosphorescent efficiency than the N,N-chelate 3a. Although 3a and 3b show bright and fluoride-switchable phosphorescence at ambient temperature, they are not dual emissive and show only metal-to-ligand chage-transfer-based phosphorescence. The nonconjugated donor-acceptor geometry and the overlap of the donor and acceptor singlet and triplet excitation bands in Si-BNPA and its Pt^{II} complexes may thus be the key for achieving singlet-triplet dual emission on two separated chromophores in a single molecule.

Introduction

Triarylboron compounds have recently found use in a wide range of functional materials due to the empty p_{π} orbital on the boron centre.^[1-4] When protected from nucleophilic attack by bulky aryl groups such as mesityl, the electron-deficient boron atom can act as a highly effective electron acceptor. Because of this, triarylboron compounds have been used successfully as nonlinear optical materials,^[1] efficient fluorescent emitters and charge transport materials in organic light emitting diodes (OLEDs),^[2] and highly selective sensors for small anions such as fluoride.^[3,4] When such compounds contain an electron-donor group, donor–acceptor charge-transfer luminescence is commonly observed.^[2-4] We have shown recently that when the donor and acceptor groups are spatially separated, the binding of fluoride ions to the boron centre interrupts this charge transfer, activating alternative emission pathways, such as $\pi \rightarrow \pi^*$ transitions, and enabling the use of these compounds as switch-on sensors for fluoride.^[4d,e]

In some triarylboron compounds, simultaneous emission from both charge transfer and $\pi \rightarrow \pi^*$ emission pathways can be observed.^[4e] Dual emissive materials are highly sought after, due to their potential as highly sensitive ratiometric sensors and as broad-band or white light emitters in OLEDs.^[5-6] Despite their importance and potential, dual emissive small molecules remain rare, in part because the molecular design requirements of such molecules are not well understood. We have shown earlier that it is possible to achieve dual fluorescent emission in organoboron com-



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pounds by control of the donor-acceptor geometry.^[4e] Furthermore, we and others have recently demonstrated that when attached to the backbone of a chelate ligand in a metal complex, a triarylboron group can greatly facilitate phosphorescent emission by metal-to-ligand charge transfer.^[7] Hence, with appropriate choice of donor and acceptor groups and their relative geometry, it may be possible to achieve singlet-triplet or triplet-triplet dual emission in a metal-containing donor-acceptor organoboron compound. Based on this principle, we have designed and synthesised a new donor-acceptor triarylboron molecule Si-BNPA (1), which contains a BMes₂ acceptor and an N-(2'-pyridyl)-7azaindolyl (NPA) donor that are linked together by a SiPh₄ group. This molecule was found to form Pt^{II} complexes readily with switchable N,N- and N,C-chelate modes. More importantly, Si-BNPA and its Pt^{II} complexes all display persistent singlet-triplet dual emission at either 77 K or ambient temperature that is also responsive to fluoride anions. The details of our investigation are reported herein.

Results and Discussion

Synthesis and reactivity of Si-BNPA and BNPA: Si-BNPA was synthesised by Suzuki-Miyaura cross-coupling of $SiPh_2(p-C_6H_4BMes_2)[p-C_6H_4B(OH)_2]$ with N-[2-(5-Br)-Py]-7-azaindole by using $SiPh_2(p-Ph-Br)_2$ as the starting material, according to Scheme 1 (see the Supporting Information for details). BNPA was synthesised according to a procedure reported recently by us.^[7d]

Si-BNPA (1) reacts readily with $[{PtPh_2(SMe_2)}_n]$ (n=2,3) to produce complex $[Pt(N,N-Si-BNPA)Ph_2]$ (2a), which can then be converted quantitatively to the "roll-over" C-H activation product [Pt(N,C-Si-BNPA)Ph(SMe₂)] (2b) upon heating in the presence of a donor ligand such as SMe₂ (Scheme 2). Complex 2b can also be obtained directly from the reaction of **1** with $[{PtPh_2(SMe_2)}_n]$ at extended reaction times at ambient temperature. The facile and quantitative conversion of the N,N-chelate complex 2a to the N,C-chelate complex 2b was monitored by ¹H NMR experiments (see the Supporting Information). These confirmed that the conversion of 2a to 2b follows the same intramolecular "roll-over" C-H activation mechanism established for the conversion of the NPA complex $[Pt(N,N-NPA)R_2]$ to [Pt-(N,C-NPA)(L)R reported recently by our group.^[8] Thus, the





b)

B(OH)₂

(BrNPA), [Pd(OAc)₂], SPhos, K₃PO₄, toluene/EtOH, H₂O (3:1:1), 90 °C, overnight.



Scheme 2. The synthetic procedures for the Pt^{II} complexes.

functionalisation of the NPA chelate with silane or triarylboron groups has little impact on its reactivity with Pt^{II}. Nonetheless, this facile N,N- to N,C-chelate mode switch provides an opportunity to study the impact of chelate mode on the emission of complexes of Si-BNPA.

To establish the impact of donor-acceptor geometry on the luminescent properties of N,N- and N,C-chelate Pt^{II} complexes based on the NPA chromophore, we also investigated Pt^{II} complexes of BNPA, which contains a BMes₂ acceptor directly conjugated to an NPA donor group. The BNPA molecule displays a similar reactivity toward the Pt^{II} ion as Si-BNPA and NPA, and as a result, complexes [Pt- $(N,N-BNPA)Ph_2$] (**3a**) and $[Pt(N,C-BNPA)Ph(SMe_2)]$ (**3b**) were obtained in the same manner as 2a and 2b (Scheme 2).

The crystal structures of 1, 2a and 3b have been determined by single-crystal X-ray diffraction analysis^[9] with 2a and **3b** shown in Figures 1 and 2, respectively. The crystal data of 1 is provided in the Supporting Information. The

> coplanar, while the structures of 2a and 3a show the {Pt(N,N-NPA)} chelate to be highly strained and puckered out-ofplane. The poor stability of the

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Figure 1. A diagram showing the molecular structure of 2a with 50% thermal ellipsoids.



Figure 2. A diagram showing the structure of $\mathbf{3b}$ with 50% thermal ellipsoids.

six-membered non-planar N,N-chelate ring thus provides the driving force for the facile transformation of **2a** and **3a** to the more stable five-membered N,C-chelate complexes **2b** and **3b**, respectively. This structural difference was also found to have a significant impact on the photophysical properties of the complexes. The separation distance between the B atom and the Pt atom in **2a** was found to be 14.8 Å.

Luminescent properties *Ligands*: Both BNPA and Si-BNPA are fluorescent with $\lambda_{max} = 392$ ($\Phi = 0.25$) and 405 nm (0.12), respectively, in THF at ambient temperature. The emission of BNPA was assigned to an NPA \rightarrow B charge-transfer transition, based on its quenching response upon the addition of fluoride (NBu₄F, TBAF).^[7d] To establish the origin of the Si-BNPA emission, we also conducted fluoride titration experiments in both absorption and emission modes. The 405 nm emission peak of Si-BNPA was quenched by F⁻ with the appearance of a new emission peak at 362 nm, as shown in Figure 3. This "turn-on" response has some resemblance to that of SiPh₂(*p*-Ph-BMes₂)[*p*-biphenyl-*N*(1-naph)Ph] reported previously by us, in which F⁻ ions quench a very weak N \rightarrow B charge transfer shoulder band and enhance a π - π *



Figure 3. The fluorescent titration spectra of **1** $(1.0 \times 10^{-5} \text{ M})$ by TBAF (0-1.8 equiv) in CH₂Cl₂ at 298 K ($\lambda_{ex} = 300 \text{ nm}$). Inset: The excitation peaks of **1** ($\lambda_{em} = 405 \text{ nm}$) and **1** + excess F⁻ ($\lambda_{em} = 360 \text{ nm}$).

transition band on the p-biphenyl-N(1-naph)Ph donor group.^[4e] Hence, it is tempting to assign the fluorescent emission of Si-BNPA to NPA \rightarrow B charge transfer. However, careful comparison of the spectra of Si-BNPA with that of $SiPh_2(p-C_6H_4-BMes_2)_2$, $(Si-BB)^{[4f]}$ which lacks a donor group, suggests that the emission of Si-BNPA most likely originates from Mes \rightarrow B charge transfer localised on the phenyl-BMes₂ chromophore. This assignment can be made given that the emission of Si-BNPA and Si-BB are identical in energy, shape and response to solvent polarity (see S5.3 and S5.4 in the Supporting Information). To establish the origin of the singlet emission of the fluoride adduct, we synthesised and recorded the emission spectrum of SiPh₃(p-C₆H₄-NPA), lacking a BMes₂ acceptor group. The emission spectrum of this molecule matches perfectly with that of the fluoride adduct of Si-BNPA (see S5.4 in the Supporting Information), confirming that the emission of the fluoride adduct can be assigned to an NPA-based π - π * transition. The "switch-on" response of Si-BNPA toward fluoride can thus be explained by the presence of distinct emission pathways on the NPA donor and boron acceptor chromophores. Emission from the acceptor is turned off by F⁻, activating the singlet emission from the donor group as the next lowest energy transition in the molecule. These assignments are further supported by TDDFT calculations at the B3LYP/6-31+ G* level of theory (see the Supporting Information).^[10]

Also significant was the observation of well-separated singlet and triplet emission peaks from SiBNPA in solution at 77 K, as shown in Figure 4 (λ_{em}^{F} =363 nm, λ_{em}^{P} =463 nm, τ^{P} = 2.2 s in THF). The singlet peak responds to F⁻ at 77 K in much the same manner as at ambient temperature, while the phosphorescent peak does not change significantly with fluoride addition (Figure 4 and Supporting Information). Also, the shape and energy of the triplet peak are similar to



Figure 4. The normalised full emission and excitation spectra of 1 (1.0×10^{-5} M) in THF at 77 K. For comparison, the emission spectrum of 1 + excess TBAF in THF with $\lambda_{ex} = 320$ nm at 77 K is also shown.

the phosphorescent peak of NPA at 77 K. Thus, the singlet and triplet peaks of 1 may be assigned to the BMes₂ and NPA groups, respectively. The excitation profiles for both singlet and triplet emission peaks at 77 K are essentially identical as shown in Figure 4, supporting that the dual emission is indeed from the same molecule. Because of this dual emission with long-lived green phosphorescence, compound 1 emits white light at 77 K under UV irradiation in solution and the solid state, which switches to a bright green emission when the UV light is turned off (Figure 5). In contrast, BNPA does not show dual emission at all under the same conditions. These results indicate that the electronic separation of the donor and acceptor chromophores as well as their well-matched excitation energies are the keys to achieving well-resolved singlet-triplet dual emission from a single molecule. Though this dual emission is both interest-



Figure 5. Comparison of the full emission spectra of **1** at 77 K and its Pt complexes at 298 K in THF. Inset: Photos of **1**, **2a** and **2b** in the solid state (UV-lamp, 365 nm).

ing and unusual, the 77 K temperature required is certainly not ideal for most applications. Fortunately, this can be addressed by chelation of a Pt^{II} centre to facilitate the triplet emission at ambient temperature.

Complexes 2 a and 2 b: As shown in Figure 5, both N,N- and N,C-chelate complexes 2a and 2b display dual emission at ambient temperature in solution, but with a distinct difference. Our data reproducibly show that the dual emission of **2a** is dominated by the singlet peak $(\lambda_{em}^{F}=399 \text{ nm} \text{ with a})$ shoulder at ~362 nm) with a very weak triplet emission peak $(\lambda_{em}^{P} = 494 \text{ nm}, \tau = 12.2(1) \text{ } \mu\text{s} \text{ at } 298 \text{ } \text{K}, 65(2) \text{ } \mu\text{s} \text{ at }$ 77 K), while the more stable, planar N,C-chelate 2b shows a similar singlet peak at λ_{max}^{F} = 392 nm with a shoulder at ~348 nm and strong green phosphorescence at $\lambda_{em}^{P} = 495$ nm $(\tau = 12.1(1) \ \mu s \ at \ 298 \ K, \ 43(2) \ \mu s \ at \ 77 \ K)$. The phosphorescent quantum yield of **2b** ($\Phi^{P}=0.025$) is much greater than that of 2a (0.007). Clearly the drastic decrease of the triplet decay lifetime from 2.2 s in the free ligand to less than 100 µs in the complexes is responsible for the observation of phosphorescence at ambient temperature. As observed in Si-BNPA, the λ_{max} and the excitation profiles for both singlet and triplet emission peaks of 2b are nearly identical except that the triplet excitation peak has a broad shoulder (Figure 6). For 2a, the excitation bands of the singlet and triplet emissions overlap, with the broad triplet excitation band being shifted considerably to a longer wavelength (Figure 7). Nonetheless, the dual emission peak profiles of 2a and 2b do not change notably with excitation energy (300–350 nm). Thus, we are confident that the dual emission is from a single molecule that shares similar excitation energy.

To confirm the origin of the dual emission peaks in 2a and 2b, we conducted fluoride titration experiments in both absorption and emission modes. The absorption spectral change with F^- for both complexes is similar to that of 1,



Figure 6. The excitation (298 K) and emission spectra of 2b and its F⁻ adduct in THF at 298 and 77 K, respectively.



Figure 7. Excitation (298 K) and emission spectra of ${\bf 2a}$ and its F^- adduct in THF at 298 and 77 K, respectively.

and the saturation point is reached with ≈ 1.5 equivalents of F⁻. Because of the extremely high sensitivity of the triplet emission peak toward oxygen for both complexes, it is very difficult to obtain quantitatively meaningful titration data in emission mode. Nonetheless, the general trends revealed by our fluoride experiments are useful in the assignment of the emission spectra. As shown in Figures 6 and 7 (full titration data are provided in Supporting Information), addition of fluorides to either 2a or 2b quenches the singlet peak while enhancing the higher-energy shoulder band in the same manner as the free ligand Si-BNPA. Thus, the singlet emission of 2a and 2b can be assigned to mesityl \rightarrow B charge transfer, while that of their fluoride adducts may be assigned to NPA-based ${}^{1}\pi \rightarrow \pi^{*}$ transitions. At 77 K, the emission spectra of 2a, 2b and their F⁻ adducts are composed almost entirely of phosphorescent emission, due to the large decrease in phosphorescent quenching at low temperature. Furthermore, the 77 K triplet peaks have well-resolved vibrational features resembling those of NPA, and thus can be assigned to an NPA-centred ${}^{3}\pi \rightarrow \pi^{*}$ transition (Figures 6 and 7). For comparison, the dual emission spectra of 1 at 77 K and 2a and 2b at 298 K are shown together in Figure 5.

It is worth noting that at ambient temperature, while the phosphorescent band of **2a** does not have a significant response to fluorides, that of **2b** experiences a huge intensity gain with the addition of ~2 equiv F⁻, changing the emission colour from pale green to bright yellow-green (Figure 8). The phosphorescent intensity gain of **2b** with fluoride can be explained as follows. First, fluoride switches the lowest energy singlet transition from BMes₂ to the ${}^{1}\pi \rightarrow \pi^{*}$ transition of the NPA group. Since the triplet emission is NPA-centred ${}^{3}\pi \rightarrow \pi^{*}$ excited state increases the population of the NPA ${}^{3}\pi \rightarrow \pi^{*}$ excited state in the metal complex promoted by the Pt^{II} centre, thus enhancing the overall emission inten-



Figure 8. The emission spectral change of ${\bf 2b}$ with TBAF (0 to 2 equiv) in $CH_2Cl_2~(1.0\times 10^{-5}\,{\rm M})$ under $N_2~(\lambda_{ex}{=}310$ nm). Inset: photos showing the colour change of ${\bf 2b}$ before and after F^- binding.

sity of the triplet peak. This same phenomenon was not observed in **2a**, perhaps owing to the much weaker phosphorescence. Although the mechanistic details of this unusual singlet-triplet dual emission require more thorough experimental and theoretical work, our preliminary data have established that the Pt^{II} ion facilitates phosphorescence through the well-known "heavy atom effect,"^[11] such that the singlet-triplet dual emission becomes visible at ambient temperature. Furthermore, the chelate mode has been shown to have a significant impact on the relative ratio of the singlet and triplet emission peaks.

Complexes 3a and 3b. The contrasting photophysical properties of the linearly conjugated complexes 3a and 3b further illustrate the importance of electronically separating the donor and acceptor chromophores to achieve dual emission in a single molecule. As shown in Figure 9, the emission of 3a and 3b at 298 K consists of a single phosphorescent band at $\lambda_{max} = 543$ nm, $\tau = 25.0(1) \,\mu$ s for 3a and $\lambda_{max} = 535$ nm, $\tau = 11.9(1)$ us for 3b. Consistent with complexes of 2, the *N*,*C*-chelate complex 3b has a much greater quantum



Figure 9. The emission spectra of **3a** (λ_{ex} =360 nm) and **3b** (λ_{ex} =368 nm) at 298 K in CH₂Cl₂ (1.0×10⁻⁵ M) with and without F⁻. Inset: photos showing the colour change of **3b** before and after F⁻ addition.

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efficiency (0.032) than the N,N-chelate 3a (0.004). However, unlike 2a and 2b, in which the triplet emission originates from the NPA chelate, the lack of any vibrational features in the emission band of 3a and 3b indicates that phosphorescence in these complexes is ³MLCT (metal-to-ligand charge transfer) in nature. Thus, direct conjugation of the electron-deficient BMes₂ group with the NPA moiety is believed to play a key role in facilitating this charge-transfer transition. Furthermore, addition of fluorides to either 3a or **3b** quenches this emission pathway with the appearance of a new phosphorescent band at a shorter wavelength (λ_{max} = 487 nm, **3a**, $\lambda_{\text{max}} = 480$ nm, **3b**) that resembles the corresponding phosphorescent bands of 2a and 2b. These can thus be assigned to N,N-NPA and N,C-NPA ${}^{3}\pi-\pi^{*}$ transitions, respectively (see Supporting Information). This phosphorescent switching changes the emission colour of solutions of 3a and 3b from yellow to green (Figure 9). The proposed switching mechanisms for the conjugated 2b and nonconjugated **3b** complexes are illustrated in Scheme 3.



Scheme 3. The proposed emission pathways and the most likely switching mechanisms by F^- in **2b** and **3b**.

Conclusions

Herein we have reported the syntheses of the first examples of luminescent metal-containing, non-conjugated donor-acceptor triarylborane compounds. Furthermore, we have demonstrated that persistent singlet-triplet dual emission in organoboron compounds can be achieved in solution at ambient temperature. This is possible through the use of both spatially separated chromophores that share a common excitation energy and metal chelation to facilitate phosphorescence. In addition, we have established that N,N- to N,Cchelate mode switching can further increase the phosphorescent efficiency of these complexes by the relief of ring strain, providing a means by which the ratio of singlet-totriplet emission may be controlled. Lastly, we have shown that the singlet-triplet dual emission in the non-conjugated system can be perturbed selectively by fluoride ions through binding to the boron receptor site, thus providing a new strategy for the development of sensing systems based on singlet-triplet switching.

Experimental Section

All reagents were purchased from Aldrich chemical company and used without further purification. DMF, THF, Et₂O, and hexanes were purified by using an Innovation Technology Co. solvent purification system. CH2Cl2 was freshly distilled over P2O5 prior to use. Reactions were carried out under an inert atmosphere of dry N2 unless otherwise stated. Thin-layer and flash chromatography were performed on silica gel. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400, 500 or 600 MHz spectrometers. Deuterated solvents were purchased from Cambridge Isotopes and used without further drying. Excitation and emission spectra were recoded using a Photon Technologies International Quanta-Master Model 2 spectrometer. Phosphorescence spectra and phosphorescent decay lifetimes were measured on a Photon Technologies International Phosphorimeter (Time-Master C-631F). UV/Visible spectra were recorded on an Ocean Optics CHEMUSB4 absorbance spectrophotometer. Cyclic voltammetry experiments were performed with a BAS CV-50W analyser with a scan rate of 0.2–1.0 V s⁻¹ using \approx 5 mg sample in dry DMF (3 mL). The electrochemical cell was a standard three-compartment cell composed of a Pt working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode. CV measurements were carried out at room temperature with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte, with ferrocene/ferrocenium as internal standard ($E^{\circ}=0.55$ V). High-resolution mass spectra were obtained with internal calibrants on an Applied Biosystems/MDS-Sciex OSTAR XL mass spectrometer in electrospray mode. Crystal structures were obtained at 180 K using a Bruker AXS Apex II X-ray diffractometer (50 kV, 30 mA, MoKa radiation). Photoluminescent quantum yields were measured using the optically dilute method ($A \approx 0.1$) at room temperature. Fluorescent quantum yields were measured in CH2Cl2 relative to anthracene ($\Phi_{\rm r}$ =0.36), while phosphorescent quantum yields were measured in degassed CH₂Cl₂ relative to fac-[Ir(ppy)₃] (Φ_r =0.4; ppy₃=2phenyl pyridine anion).^[12] Molecular orbital and molecular geometry calculations were performed using the Gaussian 03 program suite^[10] by using crystal structures as the starting point for geometry optimisations where possible. Calculations were performed at the B3LYP level of theory using $6-31+G^*$ as the basis set for all atoms except Pt, for which LAN2LDZ was used. (N-2'-(5'-Bromopyridyl)-7-azaindole)^[13] and (p-dimesitylboronylphenyl)(p-bromophenyl)diphenylsilane^[4e] were synthesised by our previously reported procedures. [{ $PtPh_2(SMe_2)$ }], $(n=2 \text{ or } 3)^{[14]}$ was prepared by methods described in the literature. Compounds BNPA and 3a were synthesised according to previously published procedures.^[7d] The synthetic and characterisation details of Si-BNPA (1). 2a and 2b. crystal structural data of 1, 2a and 3b, luminescence and DFT computational data are provided in Supporting Information.

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