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TICT fluorescence of *N*-borylated 2,5-diarylpyrroles: a gear like dual motion in the excited state†

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A significantly red-shifted fluorescence and a high fluorescence quantum yield for the emission from the twisted intramolecular charge transfer (TICT) state are attained in new aminoboranes, *N*-borylated 2,5-diarylpyrroles. A gear like dual structural motion in the excited state is responsible for their large Stokes shifts.

In the design of new π -electron materials, incorporation of main group elements into the π -conjugated carbon skeleton is a powerful strategy for creating intriguing photophysical and electronic properties.^{1,2} In particular, an attractive strategy is to make use of the synergistic effects of two or more main group elements, which enables the construction of unprecedented π -conjugated skeletons with unusual electronic structures.^{2–8} In this regard, the combination of boron and nitrogen, complementary to each other in terms of their electron-accepting/donating abilities, is of particular interest. Recent intensive efforts have produced various kinds of fascinating N–B bond-containing π -conjugated compounds.^{5–12}

Concerning the N–B bond-containing π -electron systems, a notable property is the unusual fluorescence of simple aminoboranes.^{9–12} For example, Ph₂N–BMes₂ shows absorption (λ_{abs}) and emission maxima (λ_{em}) at 282 and 456 nm, respectively, in which the Stokes shift exceeds 13 500 cm⁻¹.⁹ *N*-Dimesitylborylpyrrole **1** (Fig. 1) also exhibits an emission with a significantly large Stokes shift of 13 100 cm⁻¹.¹¹ Theoretical studies suggested that these fluorescences can be rationalized by considering the emission from the twisted intramolecular charge transfer (TICT) state.^{11*b*,13,14} The emission properties with such large Stokes shifts are highly attractive as the fluorescent dyes. However, as is usual for the TICT system, their quantum yields are low. This is due to the

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Fig. 1 Borylpyrroles: (a) known derivatives and (b) a gear like structural motion in the excited state.

reduced value of the transition moment, resulting from a small overlap of the π orbitals in the highly twisted molecular structure.¹⁵ A rational design to attain the TICT emission with a large Stokes shift and a high quantum yield at the same time remains a challenge in this field.^{16,17}

As a clue to solving this issue, we now focus on the fact that a benzene-fused derivative, *N*-borylindole **2**, can show fluorescence with a relatively high $\Phi_{\rm F}$ of 0.27 as well as an associated large Stokes shift of 10 600 cm⁻¹ in CH₂Cl₂.¹² This fact suggests that appropriate structural modification should enable the improvement of the fluorescence properties. Therefore, we decided to study the structure–property relationship for a series of new aminoboranes, including *N*-boryl-substituted carbazoles **3** and pyrroles **4–7**. Our idea for the design of these molecules was to extend the π -conjugation in the excited state to enhance the ICT character. We found that some of these molecules exhibit intriguing fluorescence based on a gear like dual structural change in the excited state (Fig. 1).

N-Borylcarbazoles **3a** and **3b** with different diarylboryl groups were synthesized by lithiation of carbazole with *n*BuLi in THF followed by treatment with the corresponding diaryl-fluoroboranes, as shown in Scheme **1**. The synthesis of *N*-boryl-2,5-diarylpyrroles **4**–7 was carried out in refluxing toluene or xylene by the reaction of the corresponding *N*-lithiated diarylpyrroles with dimesitylfluoroborane. High temperature conditions were necessary to complete the reaction, presumably due to the bulkiness of the 2,5-diarylpyrrole

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Scheme 1 Synthesis of N-borylated carbazoles and pyrroles.



Fig. 2 ORTEP drawings of (a) **3a** and (b) **4** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and torsion angles (°): (a) B1–N1 1.442(3), C1–N1–B1–C7 23.14(8). (b) B1–N1 1.472 (7), C4–N1–B1–C16 28.6(5), C1–N1–B1–C25 41.1(5), N1–C1–C5–C6 76.1(6), N1–C4–C9–C10A 58.3(12).

frameworks. These compounds were isolated by silica gel column chromatography in air.

Among the produced compounds, the structures of 3a and 4 were determined by X-ray crystallographic analysis, as shown in Fig. 2. Whereas the N-B bond moiety generally prefers to take a planar conformation due to its partial zwitterionic double bond character, these compounds take a slightly twisted conformation. The dihedral angles between the boron plane and the carbazole or pyrrole rings are 23.2 and 36.6° for 3a and 4, respectively. Compound 4 has a more twisted conformation due to the heavier steric congestion between the mesityl groups on the boron atom and the thienyl groups on the pyrrole. In conjunction with this, the dithienylpyrrole moiety takes a highly twisted conformation, in which the dihedral angles between the thiophene and pyrrole rings are 60.3 and 77.5°. The N-B bond lengths in 3a and 4 (1.442(3) and 1.472(7) Å, respectively) are slightly elongated compared to a typical N-B bond length (e.g. Me₂N-BMe₂, 1.403(1) Å),¹⁸ indicative of the weaker N-B double bond character in these sterically congested molecules.

Table 1 Photophysical data for borylated carbazoles and pyrroles 3–7

Compd	Solvent	Absorption $\lambda_{abs}/nm^a (\log \varepsilon)^b$	Fluorescence $\lambda_{\rm em}/{\rm nm} \left(\Phi_{\rm f} \right)^c$	Stokes shift $\Delta \lambda / \mathrm{cm}^{-1}$
3a	Cvclohexane	320 (4.12)	439 (0.13)	8500
	THF	320 (4.13)	455 (0.33)	9300
3b	Cyclohexane	369 (3.75)	603 (0.03)	10 500
	THF	367 (3.77)	646 (<0.01)	11 800
4	Cyclohexane	351(sh) (3.26)	626 (0.07)	12 500
	THF	349(sh) (3.29)	657 (0.02)	13 400
5	Cyclohexane	342(sh) (3.34)	514 (0.59)	9800
	THF	337(sh) (3.35)	550 (0.37)	11 500
6	Cyclohexane	379(sh) (3.27)	641 (0.06)	10 800
	THF	383(sh) (3.32)	686 (<0.01)	11 500
7	Cyclohexane	357(sh) (3.29)	502 (0.45)	8100
	THF	356(sh) (3.30)	525 (0.37)	9000

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^{*a*} Only the longest absorption maximum wavelength is given. The peak top of the shoulder band is determined by a Peak Fit program. ^{*b*} Molar extinction coefficient at the λ_{abs} . ^{*c*} Absolute fluorescence quantum yield determined by an integrating sphere system.



Fig. 3 UV-vis absorption (dashed lines) and fluorescence spectra (solid lines) of 4 (orange), 5 (green), 6 (red), and 7 (blue) in cyclohexane.

Both series of aminoboranes indeed exhibited interesting photophysical properties, which are summarized in Table 1. As a representative example, the absorption and fluorescence spectra of the *N*-borylpyrroles 4–7 in cyclohexane are shown in Fig. 3.

In the carbazole series, the Mes₂B derivative **3a** showed the λ_{abs} and λ_{em} values at 320 and 439 nm in cyclohexane with the Stokes shift of 8500 cm⁻¹.¹⁹ This value is smaller than that of Ph₂NBMes₂ (13 500 cm⁻¹ in cyclohexane), but still relatively large among compounds exhibiting TICT emissions. The incorporation of the more electron-withdrawing [2,4,6-(CF₃)₃C₆H₂]₂B group as the boron moiety resulted in a more significant red shift in the fluorescence maximum. Thus, **3b** showed an orange fluorescence with the maximum at 603 nm, which is more than 160 nm longer than that of **3a**. Its Stokes shift reached 10 500 cm⁻¹, although the fluorescence quantum yield is lower than that of **3a**. While **3a** does not show a significant solvent effect in both the absorption and fluorescence spectra, compound **3b** exhibited a red shift in λ_{em} by 43 nm

from cyclohexane to THF, indicative of its more polar character in the excited state.

A series of the N-borylpyrroles showed more characteristic photophysical properties. Thus, 2,5-dithienylpyrrole 4 possesses a weak absorption band at 351 nm as a shoulder. Upon excitation at this band, 4 exhibited a large Stokes shift of 12 500 cm⁻¹, and showed an orange emission with λ_{em} at 626 nm in cyclohexane. In more polar solvents, such as THF, its emission band further shifted to longer wavelengths with increased Stokes shifts (13 400 cm⁻¹ in THF). However, its quantum yield is only moderate even in cyclohexane. In contrast, the 2,5-diphenylpyrrole derivative 5 showed intense green fluorescence with a $\Phi_{\rm F}$ of 0.59 in cyclohexane, while maintaining a reasonably large Stokes shift (9800 cm^{-1}) for the TICT emission. We performed time-resolved fluorescence spectroscopy to determine the fluorescence lifetimes for 4 and 5, which were 8.7 and 64 ns in cyclohexane, respectively. On the basis of these values and the $\Phi_{\rm F}$ values, we determined the radiative (k_r) and nonradiative (k_{nr}) decay rate constants from the singlet excited state: $k_{\rm r} = 8.1 \times 10^6 \text{ s}^{-1}$ and $9.2 \times 10^6 \text{ s}^{-1}$ and $k_{\rm nr} = 1.1 \times 10^8 \text{ s}^{-1}$ and $6.4 \times 10^6 \text{ s}^{-1}$ for 4 and 5, respectively. The low k_r values for these compounds are consistent with the low molar extinction coefficients for their longest absorption bands. While the k_{nr} value for 4 is high, similar to other molecules possessing TICT emissions, the $k_{\rm nr}$ value for 5 is significantly low, demonstrating that the intense emission of 5 is attributable to the suppressed nonradiative decay process.

In order to further improve the TICT emission for the Nborylpyrroles, we synthesized two other derivatives 6 and 7. In the former compound, we introduced the *p*-(dimethylamino) phenyl group as an electron-donating group with a steric bulkiness similar to the phenyl group in 5. The latter compound has a sterically more congested substitution pattern with four phenyl groups at the periphery. Both compounds have the longest absorption maxima around 355-380 nm with low molar extinction coefficients. In the fluorescence spectra, the aminophenyl-substituted 6 has λ_{em} values at 641 and 686 nm in cyclohexane and THF, respectively, which are even longer wavelengths than those of the thienyl derivative 4. However, unfortunately, the $\Phi_{\rm F}$ of 6 is as low as 4. Besides, the peripherally all-phenylated 7 possesses a high $\Phi_{\rm F}$ of ~0.4, while the extent of its Stokes shift (8000–9000 cm⁻¹) is slightly smaller than that of 5.

These results provide the following notable findings: (1) Both borylcarbazoles and borylpyrroles exhibit TICT emissions with large Stokes shifts.¹⁹ In particular, (2) the electron-donating aryl-substituted *N*-borylpyrroles **4** and **6** showed reddish orange emissions with significantly large Stokes shifts. (3) The sterically more congested diarylpyrrole derivatives **5** and **7**, compared to **4**, have high $\Phi_{\rm F}$, but their Stokes shifts become somewhat smaller compared to the other derivatives. To elucidate these observations and precisely understand the behavior in the excited state, we next conducted structural optimizations of the singlet excited state for borylcarbazole **3a** and boryldithienylpyrrole **4** as the representative examples.



Fig. 4 Optimized structures for the S_0 (S_0) and S_1 (S_1 ') electronic states and an energy diagram for **3a**, calculated at the B3LYP/SV(P) level of theory.



Fig. 5 Optimized structures for the S_0 (S_0) and S_1 (S_1 ') electronic states and an energy diagram for **4**, calculated at the B3LYP/SV(P) level of theory.

Electronic structure calculations were conducted using the TURBOMOLE program package at the B3LYP/SV(P) level of theory. Excited states were treated using time-dependent density functional theory, which was shown to work well in the description of TICT states of N–B-containing compounds.¹⁴

Fig. 4 shows the optimized structures of **3a** in the ground state (S₀) and excited state (S₁') along with a schematic energy profile for both states. After vertical excitation from the S₀ Franck–Condon region to the S₁ state, a large structural change occurs upon relaxation from S₁ to the minimum of the excited state at S₁'. The major geometric change during this relaxation is the rotation around the N–B bond, combined with an increase in its bond length. Thus, the dihedral angle between the carbazole plane and the boron plane increases from 28.8° to 62.4°. In addition, the N–B bond is significantly elongated from 1.454 Å to 1.598 Å. These structural changes are similar to those already discussed for other aminoboranes.¹¹^h We also independently reported the detailed theoretical analysis of the aminoboranes.¹⁴

In contrast, the dithienylpyrrole derivative 4 shows a more complicated structural relaxation in the excited state from S_1 to S_1' , as shown in Fig. 5. According to the X-ray structural analysis, 4 has a more twisted conformation of the N–B bond in the ground state, in comparison to 3a. These structural features are well reproduced in the optimized ground state S_0

structure. The calculated N-B distance and the dihedral angle along the N-B bond are 1.482 Å and 38.5°, respectively. The calculated dihedral angles between the central pyrrole ring and the two thiophene rings are 65.9° and 66.2°. After the vertical excitation to the S1 excited singlet state, structural relaxation occurs from the Franck-Condon geometry at S1 to the minimum structure of the excited state at S₁'. The N-B bond is significantly elongated to 1.591 Å and twisted with a dihedral angle between the pyrrole ring and the boron plane of 57.8°. The degrees of the changes are comparable to those for the carbazole analogue 3a. However, it is worth noting that, in addition to these changes, the highly twisted dithienylpyrrole moiety rotates into a planar conformation. The dihedral angles between the central pyrrole and the two thiophene rings are 13.6° and 14.2°. This gear like dual motion of the twisting/stretching of the B-N bond and the planarization of the diarylpyrrole moiety stabilizes the S₁' energy level by 1.04 eV and destabilizes the S_0' energy by 0.74 eV. Notably, the degrees of these energy changes are greater compared to those for the carbazole analogue 3a. Consequently, the boryl-substituted dithienylpyrrole 4 does show the larger Stokes shift.

These quantum chemical calculations demonstrate that the fluorescences of the boryl-substituted carbazoles and 2,5-diarylpyrroles are indeed derived from the TICT state.¹⁹ In the 2,5diarylpyrroles, the dual structural motion to form the TICT state is the origin of the significant Stokes shift. In particular, the twisted conformation of the diarylpyrrole moiety in the ground state is crucial to attain the present fluorescence, because if the 2,5-diarylpyrrole skeleton has a coplanar conformation in the ground state, these compounds would only show an emission by the π - π * transition for the diarylpyrrole moiety, instead of the TICT emission of the N-B moiety. The planarization of the 2,5-diaryl moiety in the excited state at S₁' increases the electron-donating ability, since the positive charge on the N atom becomes stabilized by greater π delocalization. Therefore, the more electron-donating aryl groups, like the thienyl or *p*-(amino)phenyl groups, enhance the ICT character, resulting in the more red-shifted emission. Besides, the degree of the planarization of the 2,5-diarylpyrrole moiety in the excited state at S₁' is the other factor to attain the significant Stokes shift. The sterically congested diphenyl- or tetraphenyl-substituted compounds 5 and 7 exhibited a less significant Stokes shift. However, worth noting is that these structures realize high fluorescence quantum yields of 0.4-0.6, which is among the highest for the TICT emission. These results not only provide examples of the emissive TICT molecular systems, but also important knowledge for further molecular designs of more elaborate fluorescent molecular systems. In particular, precise control of the structural change in the excited state will be the key for further designs.

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