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Graphical Abstract

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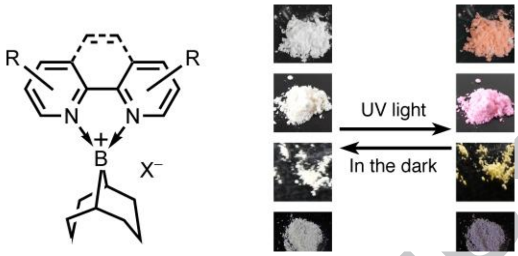

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Photoinduced solid-state coloring behavior of boronium complexes

Junro Yoshino [a], *, Tenku Sekikawa [a], Naoya Hatta [a], Naoto Hayashi [a] and Hiroyuki Higuchi [a], *

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Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

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ABSTRACT

Boronium complexes bearing a 9-borabicyclononane framework with a bipyridine-type ligand display photoinduced solid-state coloring behavior. While the identity of the substituents on the boron atom is critical to gain photoresponsive capability, modifying the nitrogen-containing ligand structure and its substituents provides a wide variation in the photoinduced solid color.

Boronium complexes bearing a bipyridine ligand can be considered as analogues of photochromic viologens and diquat,[1–3] yielded by exchanging the carbon atoms attached to the nitrogen atoms in viologens and diquat with a boron atom. A boronium salt having a viologen-like structure was reported in 2011.[4] Boronium salts bearing a 2,2′-bipyridine (bpy) moiety have been known since 1959.[5] Among them, (2,2′-bipyridine-*N*,*N*′)(cyclooctane-1,5-diyl)boronium hexafluorophosphate and its corresponding triflate (**1**, bpyBBN$^+$TfO$^-$), have a 9-borabicyclo[3.3.1]nonane (9-BBN) framework (Figure 1).[6–8] They were investigated via their UV-vis spectra in solution, chemical reduction behavior, and X-ray crystallographic analysis. Recently, generation of persistent neutral radicals [(bpy)BR$_2$]•, which are chemically reduced forms of bpy-boronium complexes, and the ESR spectra of those radicals have been reported.[9–11] More complex bpy(boronium)-based compounds have also been studied.[12,13] While the high electron-accepting character of bipyridine-based boronium ions has been intensively studied and in this character they resemble viologens and diquat, no work to date has revealed the photoresponsive nature of boronium complexes, in contrast with the extensive studies on photochromic nature of viologens and diquat. Meanwhile, organoboron compounds are expected to provide a potential repository of photoresponsive compounds. Recently, new and unique neutral organoboron systems not based on the conventional photochromic core molecular structures have been reported.[14–17] However, photoresponsive behavior of boronium complexes has been left veiled.

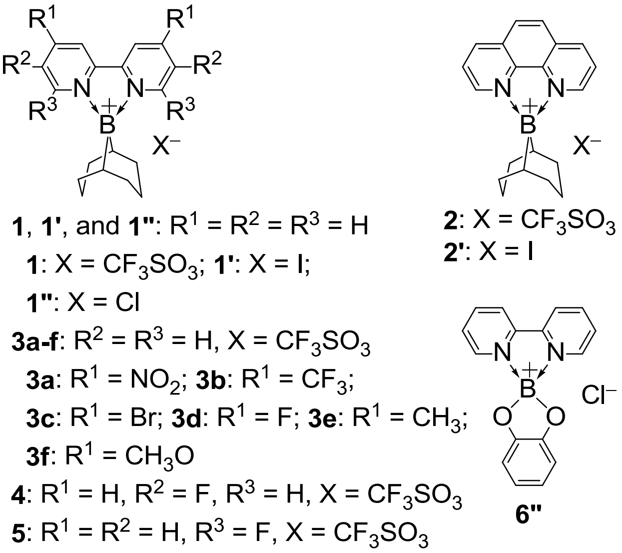

Figure 1. Boronium complexes.

In this work, we report the reversible color changes of **1** and its analogues in the solid state upon light irradiation. Elucidation of the nature of boronium complexes should help to add a new

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aspect of photoresponsive organoboron compounds, because the mechanism of their photoreactions may differ from those of known photoresponsive boron compounds due to the considerable difference of electronic structures. If a methodology to tune the photoresponsive behavior of boronium complexes can be established, organoboron compounds are expected to gain expanded functions and application opportunities as a photoresponsive material because of their facile syntheses and finely adjustable structures. Here we report the synthesis and the photoinduced solid-state coloring behavior of boronium complexes bearing a bpy moiety to reveal their structure–property relationships.

First, the spectroscopic properties of compound **1** are summarized to discuss its photoresponsive behavior. Two absorption bands are observed in the ultraviolet region of the UV-vis spectrum of **1** in acetonitrile (MeCN) (Figure 2 and Table 1). One band has maxima at 305 and 315 nm, attributed to the bpy ligand-localized π–π* transition with vibrational structure.[8] Another band appears at 330–400 nm as a broad-shaped shoulder with a small molar absorption coefficient (2 × 10^3 $M^{-1}cm^{-1}$). The diffuse reflection spectrum of **1** in the solid state is similar to the absorption spectrum in solution, especially in the absorption maxima wavelengths (Figure 2 and Table S1). The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations (calculated at the B3LYP/6-31G(d) level of theory) revealed that the lowest-energy absorption band was attributed to the HOMO–LUMO transition of bpyBBN$^+$. The HOMO and LUMO are mainly localized on the B–C/C–C σ-bonds of the BBN moiety and on the π* orbital of the bpy ligand, respectively (Figure 3). This indicates that a charge transfer (CT) from the BBN moiety to the bpy ligand occurs when this cation is excited at the wavelength corresponding to the lowest-energy transition. The bpy ligand-localized π–π* absorption can be attributed to the HOMO−3–LUMO transition. In the fluorescence spectrum, compound **1** exhibits the fluorescence maximum at 495 nm in MeCN (Figure 2 and Table S2).

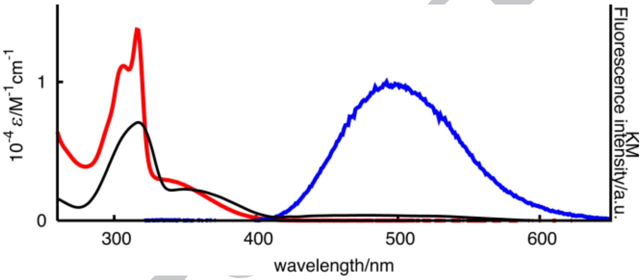


Figure 2. UV-vis absorption (red line) and fluorescence (blue line) spectra of compound **1** in MeCN, and its diffuse reflection spectrum (black line) in the solid state.

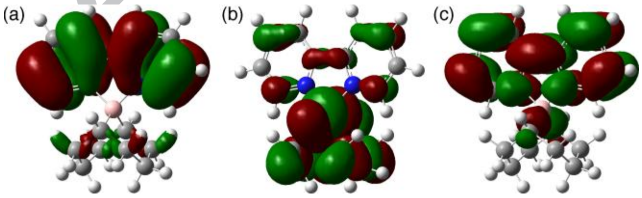


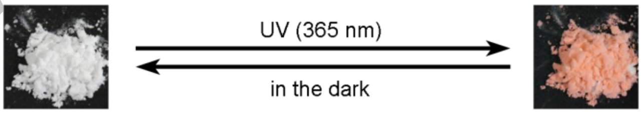
Figure 3. Molecular orbital diagrams of bpyBBN$^+$ (calculated at the B3LYP/6-31G(d) level of theory). (a) HOMO−3 (b) HOMO (c) LUMO.

Photoinduced coloring behavior of **1** was observed in the solid state. Irradiation with UV light (365 nm) of the solid of **1** afforded a color change from colorless to red-orange (Scheme 1). Its blue fluorescence was quenched concurrently with its color change. This solid-color change can be confirmed by the diffuse reflection spectra, in which a new absorption peak appears in the visible region (527 nm) after exposure to UV light (Figure 4). These visual and spectroscopic responses to the UV irradiation seem to be reversible, because the photoinduced color and new absorption peak gradually disappear after removing the UV light source, returning to the initial color and spectrum.

Table 1. Wavelengths of absorption maxima (λ_{abs}) in MeCN

compd	λ_{abs}/nm [a,b]	
	π–π*	CT
1	305 (1.1 × 10^4), 315 (1.3 × 10^4)	(335)
1′	305 (1.1 × 10^4), 315 (1.3 × 10^4)	(334)
1″	306 (1.4 × 10^4), 316 (1.7 × 10^4)	(333)
2	280 (2.0 × 10^4)	360 (1.9 × 10^3)
2′	280 (2.5 × 10^4)	363 (2.0 × 10^3)
3a	329 (1.4 × 10^4)	387 (5.5 × 10^3)
3b	312 (1.4 × 10^4), 323 (1.6 × 10^4)	361 (4.3 × 10^3)
3c	305 (1.6 × 10^4), 315 (2.0 × 10^4)	348 (5.2 × 10^3)
3d	291 (1.4 × 10^4), 302 (1.6 × 10^4)	338 (3.7 × 10^3)
3e	301 (1.4 × 10^4), 312 (1.7 × 10^4)	(330)
3f	288 (1.1 × 10^4), 299 (1.5 × 10^4)	327 (4.9 × 10^3)
4	318 (1.6 × 10^4), 326 (1.8 × 10^4)	(345)
5	316 (2.0 × 10^4), 330 (2.4 × 10^4)	(353)

[a] Wavelengths in parentheses indicate shoulders. [b] Molar absorption coefficients of maxima are given in parentheses following the wavelength.



Scheme 1. Photographs of compound **1** in the solid state before (left) and after (right) UV irradiation.[18]

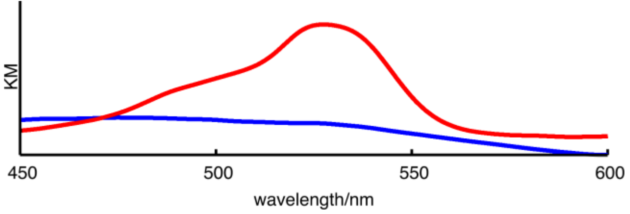


Figure 4. Diffuse reflection spectra of compound **1** in the solid state before (blue line) and after (red line) UV irradiation.[18]

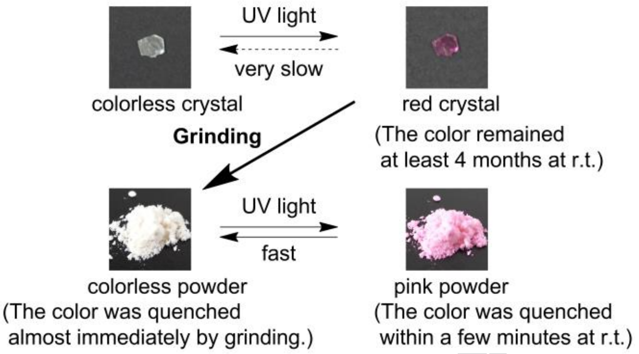
To reveal the structure–property relationships of the boronium complexes, several analogues of **1** were investigated. PhenBBN$^+$TfO$^-$ (**2**), a complex bearing 1,10-phenanthroline (phen) instead of bpy, was synthesized by a method similar to that reported for **1** (Scheme S1).[7] Iodide salts **1′** and **2′**, a chloride salt **1″**, and R_2bpyBBN$^+$TfO$^-$ **3a-f**, **4**, and **5** were also synthesized (Figure 1, Scheme S1, Table S2). These compounds were fully characterized by ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR as well as MS spectra. They are stable toward air and water both in the solid state and in solution.

UV-vis and fluorescence spectra in MeCN and diffuse reflection spectra in the solid state of **2**, **3a–f**, **4**, **5**, **1′**, **1″**, and **2′** show similar spectra to those of **1** (Figures S1–S12 and Tables 1, S1 and S2). This suggests that the electronic structures and electronic transitions of the boronium complexes with a BBN moiety are not strongly affected by the exchange of a nitrogen-containing ligand, substituents, and/or counteranion. The absorption spectra in the solution state of triflates **1** and **2** and their corresponding iodides **1′** and **2′** exhibit no large differences, indicating very weak or no interaction between the cation and anion in the solution state. In contrast, in the solid state, **1′** and **2′** show very broad and low-intensity tailing of the absorption bands at the long-wavelength side from 400—500 nm, while **1** and **2** show no such tailing bands. This suggests that the interactions between the cation and iodide anion are large compared with the triflates. X-ray crystallographic analysis of **2** and **2′** also showed that the exchange of the counteranion created some crystal-packing differences (Figures S13–S16).[19]

The wavelengths of the absorption maxima of compounds **1** and **3a–g** indicate that stronger electron-withdrawing groups at the 4,4′-positions of the bpy ligand cause larger red shifts in the absorption peaks (Table 1). Based on the DFT calculations, this substituent effect can be explained as deriving from the sufficient presence of the LUMO orbital lobe, whereas the relatively limited presence of the HOMO orbital lobe, and the absence of the HOMO−3 orbital lobe owing to the orbital node on the carbon atoms at the 4- and 4′-positions of the bpy ligand. This distribution of the molecular orbitals provides higher sensitivity of the LUMO energy level to the substituents at the 4,4′-positions than those of the HOMO and HOMO−3 (Figure 3). Thus strong electron-withdrawing groups notably lower the LUMO energy level rather than the HOMO/HOMO−3 energy levels to red–shift the absorption.[20] Comparing the absorption wavelengths of **3d**, **4**, and **5** reveals no significant absorption shifts from varying the substituent positions on the bpy ligand and only a slight red-shift of the π–π* absorption bands in the 4,4′-difluoroisomer.

The effects of the nitrogen-containing ligand's structure, substituents, and counteranion on the photoinduced coloring behavior of the boronium complexes were investigated. While changing the ligand from bpy to phen and/or the counteranion from triflate to iodide or chloride maintains the solid-state photoresponsive capability, the identity of the substituents bound to the boron atom notably affected the photoresponsivity, judging from the nonphotoresponsive nature of bpyB(catecholato)$^+$Cl$^-$ (**6″**) observed in preliminary experiments (Figure 1). In the qualitative experiments, iodide **1′** exhibits the most photosensitive nature among bpyBBN$^+$ salts **1**, **1′**, and **1″**, and chloride **1″** is second. The position and electronic properties of substituents on the bpy ligand also clearly affect the color change upon UV irradiation and provide a wide variation in the photoinduced solid color such as red, orange, yellow, and violet (Table S3).

The coloring/color-quenching behavior can be observed in both the crystal and powder forms and in all of the following atmospheres: argon, air, and oxygen. While the photoreaction seems to occur on the surface of the solid, a small part of the complex on the inside also reacts when using a large and clear crystal sample. Interestingly, the rate of the quenching of the photoinduced solid color is strongly affected by the solid form and atmosphere. Quenching is slower in the crystal than in the powder form, and grinding the solid accelerates it (Scheme 2). While quenching occurs under an argon atmosphere, it is accelerated under air or oxygen. The rate of color-quenching reaction also depends on temperature. At 203 K, the photoinduced solid color in the powder form was maintained significantly longer than at room temperature. At 423 K, quenching was completed in few seconds in the powder form, while it took several minutes at room temperature in the same conditions except for temperature. In the crystal form, acceleration of quenching at 423 K was observed, although the part of the color remained after a half-hour heating.



Scheme 2. Influence of solid form on the coloring/color-quenching behavior of compound **2**.[18]

The photochemical products were examined to reveal the mechanism of the photochemical process. However, all measurements except ESR measurments of the photoirradiated solids failed to give a hint on the photoproducts.[21] In the ESR spectrum of photoirradiated complex **2** in the solid state, a signal was observed with g = 2.00394 (Figure 5). The photoirradiated solids of **1** and **1′** also yielded ESR signals with nearly the same g values (g = 2.00437 and 2.00389, respectively). This suggests the presence of organic radical species in the photoirradiated solids of the boronium complexes. This suggestion is supported by the fact that the photoproduct can react with oxygen. A broad shaped ESR peak without hyperfine coupling suggests the presence of a relatively strong interaction between radical species and the surrounding ions in the solid-state.

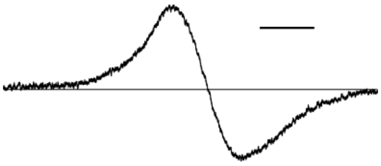
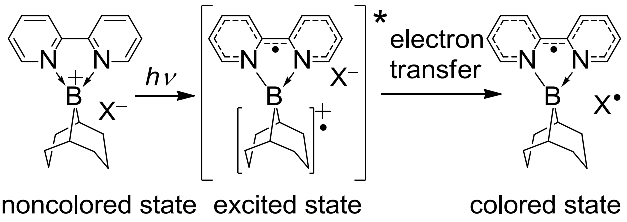


Figure 5. ESR spectrum of compound **2** in the solid state after UV irradiation. A horizontal bar indicates 1 mT.[18]



Scheme 3. Possible mechanism for photoinduced coloring.

Based on these experimental and computational results, a viologen-like photoredox process, shown in Scheme 3, is considered to be a possible mechanism for photoinduced coloring of the boronium complexes. Theoretical calculations of the lowest singlet excited state and the frontier orbitals of the cationic section of the complex support the first step of the mechanism, the reduction of the nitrogen-containing aromatic ligand by photoexcitation to form its radical. The similarity of the observed g values to the reported values of chemically reduced boronium complexes bearing a bpy ligand also supports this mechanism.[9,11] In addition, the absorption peak shown in Figure 4 attributed to the photoproduct of **1** resembles that of the radical generated from **1** with sodium in DMF according to the method reported in the literature (Figure S17).[6,22] The second step, the oxidation of the counteranion with the excited cationic section, is assumed by analogy to the mechanism of photochromism of arylviologen *p*-toluenesulfonate salts.[1,2] Although rearrangement has been observed in the case of the photochromism of tetracoordinate triarylboranes bearing an intramolecular coordination site,[14,17] it would not be so favorable in the case of the boronium complexes due to the absence of π-bonds available for rearrangement at the substituents on the boron atom and to the presence of ESR active species not expected in the rearrangement mechanism. According to this hypothesis, a sufficiently low energy level of the HOMO of the cationic moiety to oxidize the counteranion in the excited state, provided by a boryl moiety such as BBN found in the relatively strong Lewis acidic tricoordinate boron compounds, and an appropriate level of the oxidation potential of the counteranion would be required to gain photoresponsive capability in the boronium complexes. For color-quenching, the detailed mechanism is unclear and whether the transformation between the noncolored and colored states is reversible or not has yet to be determined, while an oxygen-participating irreversible reaction may mainly contribute the quenching under air/oxygen.

In conclusion, photoinduced solid-state coloring behavior of bpyBBN$^+$TfO$^-$ (**1**) and its analogues was revealed. Compound **1** itself, its phenanthroline-ligand analogue phenBBN$^+$TfO$^-$ (**2**), and their halide salt analogues **1′** , **1′′**, and **2′** exhibited reversible color change in the solid state upon UV irradiation, while bpyB(catecholato)$^+$Cl$^-$ (**6′′**) had no photoresponsive capability. Modifying the position and electronic properties of substituents on the bipyridine ligand of **1** provided wide-ranging color variation of the photoirradiated solids. Based on the experimental and computational results, a viologen-like photoredox process is suggested as a possible mechanism for photoinduced coloring. The structure–property relationships determined in this study may provide a basis for the development of novel and easily modifiable photoresponsive materials.

Acknowledgments

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Supplementary data

Supplementary data (experimental procedures, characterization data, computational studies, Table S1–3, Scheme S1, and Figures S1–17) associated with this article can be found, in the online version.

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18. All measurements and photoirradiation were perfomed under air.
19. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1453149 and 1453150. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
20. Compound **3d** shows irregularity in this trend, probably due to the ambivalent nature of a fluoro group in the inductive and mesomeric effects.
21. NMR spectra of the solutions prepared from the photoirradiated boronium complex solids showed no other peaks than those attributed to the original complex. X-ray crystallographic analysis of single crystals of the complexes after exposure to UV light also gave no indication of additional chemical species. In addition, the new absorption appearing after irradiation in the diffuse reflection spectra was very weak in comparison with the original absorption of the complex. These results suggest that the yields of the photochemical products are very low. An acetone-d_6 solution of **2** showed color change from colorless to red in 3 min upon irradiation, but no notable peaks of photoproducts could be observed by NMR. As for other conditions, solutions of **1** and **2** do not necessarily show color change. In all cases, prolonged irradiation in the solution state resulted in irreversible decomposition of the complexes. In the case of **2** in acetone, there is a possibility of the occurrence of a reaction similar to that in the solid state, but what occurs here is still unclear.
22. Both peaks appear in the visible region with a broad shape. The absorption of the photoproduct in the solid state is somewhat red-shifted from that of the radical in DMF. This shift could be attributed to differences in the state of the radicals, in solution or in the solid.

Highlights

Bpy-boronium complexes display photoinduced solid-state coloring behavior.

The substituents on the boron atom is critical to gain photoresponsive capability.

Modifying the ligand provides a wide variation in the photoinduced solid color.

A viologen-like photoredox process is suggested as a possible mechanism for coloring.