



Photoinduced solid-state coloring behavior of boronium complexes



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ARTICLE INFO

Article history:

Received 16 September 2016

Revised 19 October 2016

Accepted 24 October 2016

Available online 24 October 2016

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

Keywords:

Boronium complex

Photoreaction

Photoresponsive coloring

Solid-state reaction

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.

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Introduction

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 (Fig. 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)BR₂][•], 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.

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 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) (Fig. 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 ($2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The diffuse reflection spectrum of **1** in the solid state is similar to the

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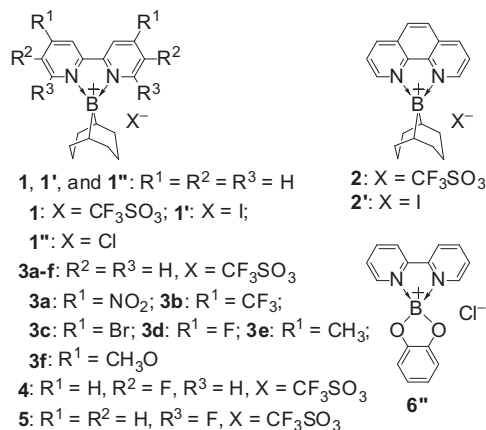


Fig. 1. Boronium complexes.

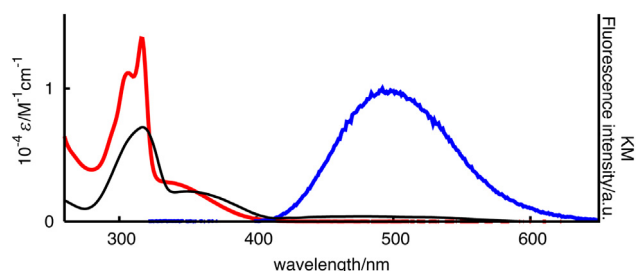


Fig. 2. UV-vis absorption (red line) and fluorescence (blue line) spectra of compound **1** in MeCN, and its diffuse reflection spectrum (black line) in the solid state.

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

compd	$\lambda_{abs}/nm^{a,b}$	
	$\pi-\pi^*$	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.

absorption spectrum in solution, especially in the absorption maxima wavelengths (Fig. 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 (Fig. 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 $\pi-\pi^*$ absorption can be attributed to the HOMO–3–LUMO transition.

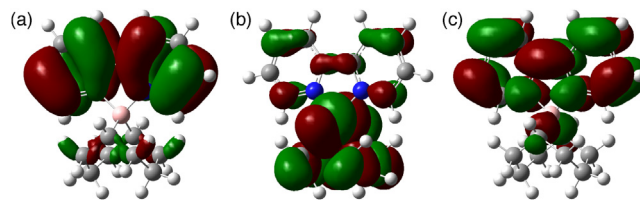
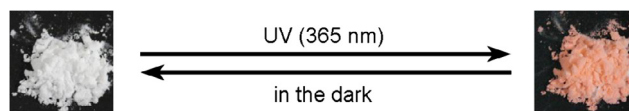


Fig. 3. Molecular orbital diagrams of bpyBBN⁺ (calculated at the B3LYP/6-31G(d) level of theory). (a) HOMO–3 (b) HOMO (c) LUMO.



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

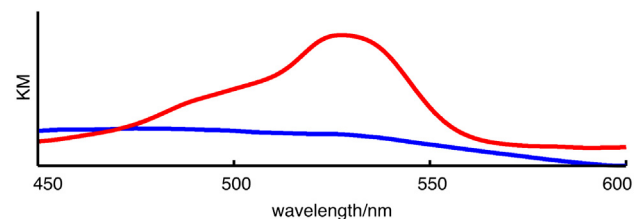


Fig. 4. Diffuse reflection spectra of compound **1** in the solid state before (blue line) and after (red line) UV irradiation [18].

In the fluorescence spectrum, compound **1** exhibits the fluorescence maximum at 495 nm in MeCN (Fig. 2 and Table S2).

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 (Fig. 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.

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 R₂bpyBBN⁺TfO[−] **3a–f**, **4**, and **5** were also synthesized (Fig. 1, Scheme S1, Table S2). These compounds were fully characterized by ¹H, ¹³C, ¹¹B, and ¹⁹F 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** (Figs. 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

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