



Preparation of fluoride anion responsive poly(*N*-vinylcarbazole)-borane complexes

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ABSTRACT

A series of novel fluoride anion responsive materials were facily prepared by complex formation of poly(*N*-vinylcarbazole) with organoboron compounds in tetrahydrofuran. After addition of fluoride anion, visual color changes of fluorescence emission from green to blue were observed. The ^{11}B NMR spectra shown that poly(*N*-vinylcarbazole)-borane complexes were converted to poly(*N*-vinylcarbazole) and fluoroborate in the presence of fluoride anion. Among the obtained poly(*N*-vinylcarbazole)-borane complexes prepared, poly(*N*-vinylcarbazole)-triethylborane complex exhibited the most distinct visual changes in fluorescence emissions.

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1. Introduction

Design of chemosensors which are capable of detecting anion sensitively has been a subject of strong interest for a long time [1–6]. Particularly, fluoride anion sensors [7–36] are being studied vigorously, because of the utility of this anion in spite of its toxicity. Fluoride ion is used in dental care or treatment of osteoporosis [37–38]. One of approaches to detect fluoride anion has been designing receptor molecule that forms hydrogen bond with fluoride anion [9–12]. As another major approach, design of arylborane type anion receptor has been widely examined [18–36]. In late 1990s, organoboron π -conjugated systems highly extended through the vacant *p*-orbital were developed by several groups independently [18–23]. After a divergently extended organoboron π -conjugated systems were reported to work as fluoride anion sensor [23–25], a variety of triarylborane based colorimetric fluoride anion sensors have been developed. In these systems, borate formation of organoboron unit with fluoride anion results in interruption of π -conjugation, which leads to blue-shift of absorption and quenching of fluorescence emission. Bidentate type borylated naphthalene derivatives [26–30] were also reported, which showed improved fluoride binding ability compared with monodentate type arylboranes. Recently, cationic triarylboranes that chelate fluoride anion in aqueous environment were also reported by Gabbai et al. [31,32]. The first phosphorescent anion sensor [33] was also reported by them. A novel turn-on type fluoride ion sensor [34] (U-shaped π -conjugated molecule in which triarylamine quenches the emission of the triarylborane unit) was also reported by Wang et al.

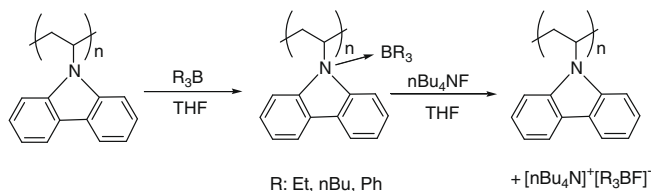
However, structures of organoboron fluoride ion sensors have been limited to boric acids or triarylboranes for a long time. In the present work, novel poly(*N*-vinylcarbazole)(PVCz)-trialkylborane complexes were examined as fluoride anion responsive materials (Scheme 1). The facily prepared PVCz-trialkylborane complexes are expected as a useful alternative to boric acids or triarylborane derivatives.

2. Results and discussions

Boron–nitrogen complexes are well known compounds as reported in early works by Brown et al. [39–41]. These compounds have been studied as valuable precursors for ceramics [42] such as boron nitride, and also as light emitting materials [43–45]. Very recently, these compounds are also investigated as a new class of electrolytes [46], which can be regarded as *pseudo* ionic liquid prepared via Lewis acid–Lewis base neutralization. From these works, it was demonstrated that boron–nitrogen complexes can behave as an interesting class of functional materials. PVCz [47] is well known as a photo-conductive material, while it exhibits a very weak fluorescence emission. However, after complex formation of PVCz with organoboron compounds, a moderate exciplex emission was observed. (Recently, novel blue light emitting polyaniline–borane complex was reported by Sarma et al. [48].)

Here, PVCz was prepared by conventional radical polymerization of *N*-vinylcarbazole using AIBN as an initiator. From the gel permeation chromatographic (GPC) analysis (chloroform as an eluent; PSt standards), the number average molecular weight of the PVCz was 5700. The PVCz–borane complexes were facily prepared by adding an equimolar amount of trialkylborane in THF to a THF solution of PVCz at room temperature and stirring the reac-

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Scheme 1. Synthesis of poly(*N*-vinylcarbazole)-borane complex and its reaction with fluoride anion.

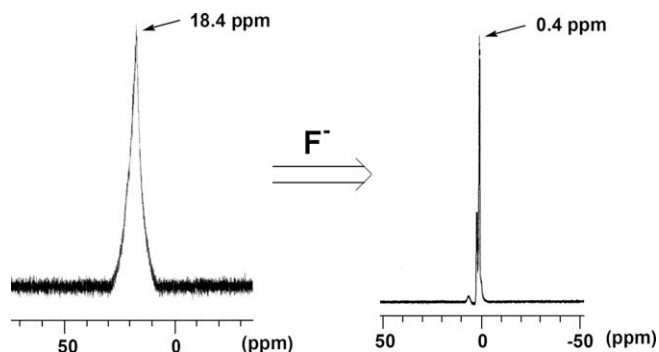


Fig. 1. ^{11}B NMR spectra (in CDCl_3) for poly(*N*-vinylcarbazole)-triethylborane complex (left; before the polymer reaction) and poly(*N*-vinylcarbazole)/borate mixture (right; after the polymer reaction).

tion mixture for 12 h. After the solvent was removed, the structures of the polymer complexes were supported by ^1H and ^{11}B NMR spectra. The polymers obtained were well soluble in common organic solvents such as THF, chloroform and DMF. In the ^{11}B NMR spectrum of PVCz–triethylborane complex, the complex formation was indicated from the observation of one main peak at 18.4 ppm (Fig. 1), which was significantly upfield shifted compared with that of triethylborane–THF complex (32.2 ppm).

After the complex formation, the absorption maxima of the polymers were largely red-shifted in the UV–Vis absorption spectra measured in CHCl_3 . PVCz–triethylborane complex showed its absorption maximum at 350 nm with the absorption edge of around 500 nm. The PVCz–borane complexes were moderately fluorescent. When a dilute chloroform solution of PVCz–triethylborane complex was irradiated at 365 nm, a green emission was observed at 471 nm ($\Phi = 1.84 \times 10^{-2}$; determined by using anthracene-9-carboxylic acid as a standard [49]). Each PVCz–borane complex was fluorescent, however, PVCz–triethylborane complex showed the highest quantum yield in chloroform at r.t. The fluorescence emission wavelength of PVCz–triethylborane complex showed a large dependence on kinds of solvents (Table 1). Since polarized excited state was stabilized in polar solvents, emission wavelength shifted to lower energy region with increasing the solvent polarity. However, the extraordinary large dependence should not be solely due to solvent polarity but also to interaction of solvents with the boron atom. The concentration dependence of fluorescence emission for PVCz–triethylborane complex was also checked in chloroform. Under the concentration range from

Table 1
Fluorescence emission wavelength^a of poly(*N*-vinylcarbazole)-triethylborane complex in various organic solvents.

Solvent	CHCl_3	CH_2Cl_2	THF	DMF
$\lambda_{\text{max}}(\text{nm})$	471	470	400	398

^a At room temperature. Excitation wavelength at 365 nm.

3.7×10^{-2} M to 5.0×10^{-4} M, no significant changes of emission maxima were observed. Therefore, the observed solvent dependence should not be due to excimer formation.

The reaction of PVCz–borane complexes with fluoride anion was examined by adding equimolar amount of tetrabutylammonium fluoride (TBAF; 1.0 M THF solution) to THF solution of PVCz–borane complexes and stirring the reaction mixtures at r.t. After the reaction, the main peak of ^{11}B -NMR of the polymer solution shifted to upperfield region. For instance, the main peak for PVCz–triethylborane complex at 18.4 ppm shifted to 0.4 ppm (Fig. 1). After the addition of TBAF, the peak at 18.4 ppm had completely disappeared, indicating a quantitative conversion of Cz–borane complex to a borate.

In the UV–Vis absorption spectrum of the polymer after the addition of TBAF, the absorption maximum was largely blue-shifted (Fig. 2a). The shape of the spectrum was quite similar with that of PVCz before the complex formation with triethylborane (Fig. 3). This indicates that the polymer complex was converted to PVCz.

Drastic changes were also observed in the fluorescence emission spectra. After treated with TBAF, the emission maximum of PVCz–triethylborane shifted from 471 nm (green) to 420 nm (blue) with decreasing its intensity (Fig. 2b). The fluorescence quantum yield (Φ) decreased from 1.84×10^{-2} to 4.68×10^{-3} (Fig. 4). Such a distinct change was observed only in the case of PVCz–triethylborane, possibly because of large steric hindrance around the boron atom in PVCz–tributylborane or PVCz–triphenylborane (Fig. 4). The photographs of fluorescence emission of PVCz–triethylborane solution before and after the TBAF addition are represented in Fig. 5. A visual change of the emission from green to blue was also observed in naked eyes.

We have also examined the measurement of fluorescence emission spectrum of PVCz–triethylborane in the presence of tetrabutylammonium bromide (TBAB). However, no significant change of emission spectra was observed, showing that this material is specific for fluoride anion detection.

In summary, facile fluoride anion detection was possible using PVCz–borane complex. Differently from PVCz which is well known as a photo-conductive material, PVCz–borane complexes were found to show moderate fluorescence emission. Addition of TBAF solution to a THF solution of PVCz–triethylborane resulted in distinct changes in both absorption and emission. The colorimetric change of the fluorescence emission from green to blue was visually observed, which demonstrated that the present system serves as a valuable fluoride anion responsive material. The quantitative reaction of PVCz–triethylborane complex with fluoride ion was observed in the ^{11}B NMR spectra, revealing that the present system is a new type of fluoride anion responsive material as a useful alternative to boric acids and arylboranes.

3. Experimental

3.1. Materials and instruments

Poly(*N*-vinylcarbazole) was prepared according to the reported method [47]. Commercially available 1.0 M THF solutions of triethylborane and tributylborane were purchased from Aldrich and used as received. Triphenylborane purchased from Aldrich was used after recrystallized from diethylether. 1.0 M THF solution of tetrabutylammonium fluoride was purchased from Tokyo Chemical Industry (TCI) Co. Ltd. and used as received. 9-Anthracene carboxylic acid purchased from Tokyo Chemical Industry (TCI) Co. Ltd. was used without further purification. THF was distilled over sodium before use. All the reactions were carried out under nitrogen atmosphere.

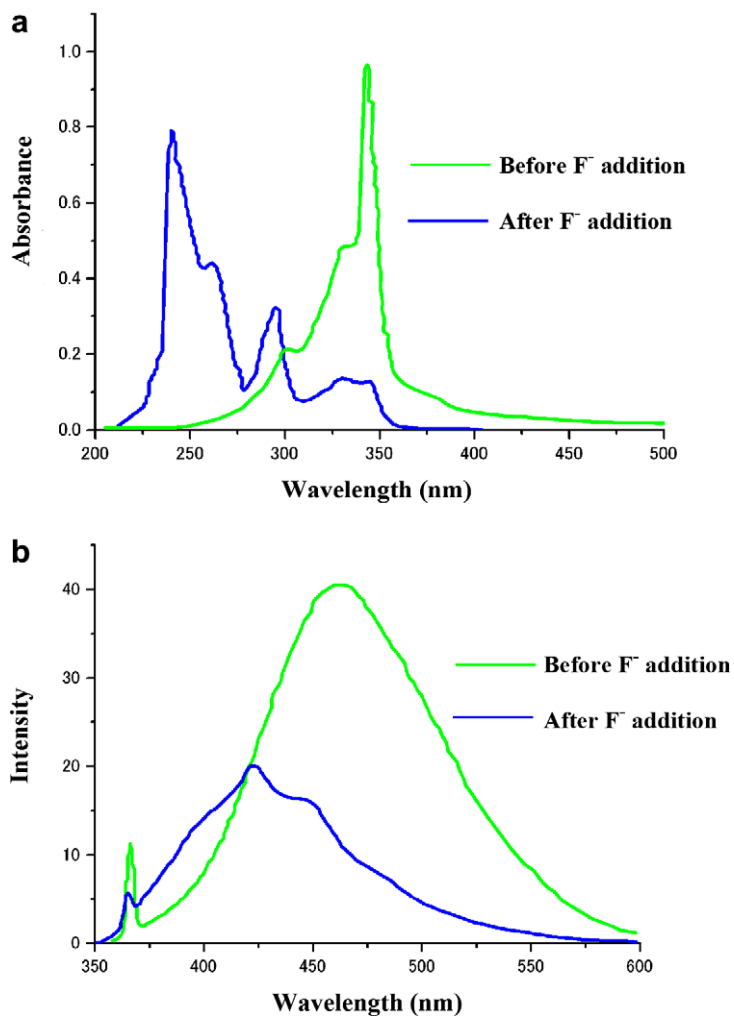


Fig. 2. (a) UV-Vis absorption spectra (in CHCl₃, at r.t.) for poly(*N*-vinylcarbazole)-triethylborane complex (green line; before F⁻ addition) and poly(*N*-vinylcarbazole)/borate mixture (blue line; after F⁻ addition). (b) Fluorescence emission spectra for poly(*N*-vinylcarbazole)-triethylborane complex (green line; before F⁻ addition) and poly(*N*-vinylcarbazole)/borate mixture (blue line; after F⁻ addition) (in CHCl₃, at r.t.; excitation wavelength at 365 nm).

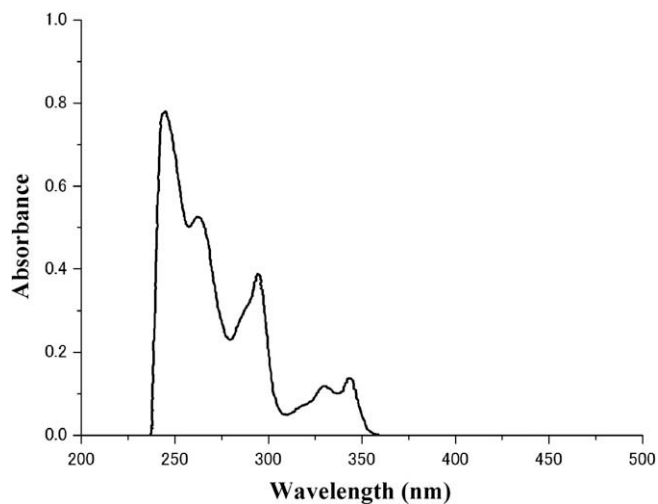


Fig. 3. UV-Vis absorption spectrum (in CHCl₃, at r.t.) for poly(*N*-vinylcarbazole).

The ¹H and ¹¹B NMR spectra were recorded on BrukerARX400 or AVANCE400s spectrometer. The UV-Vis absorption spectra were recorded on a Ubest-30 (JASCO Co. Ltd.) spectrometer. The fluores-

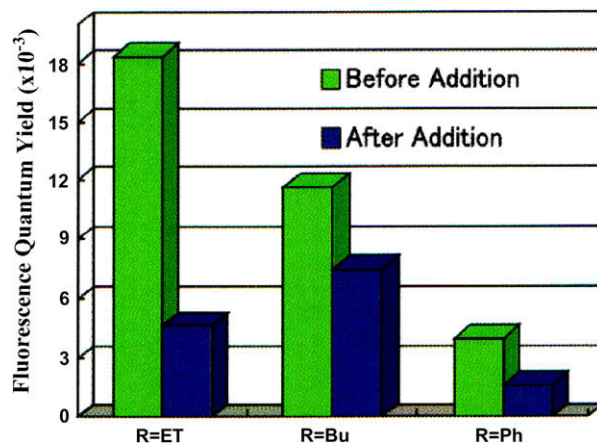


Fig. 4. Fluorescence quantum yields (in CHCl₃, at r.t.) for polymers before (green column) and after (blue column) the addition of fluoride anion.

cence emission spectra were recorded on a F-4500 (Hitachi Co. Ltd.) spectrometer. The fluorescence quantum yields were determined according to the reported method [49].



Fig. 5. The photographs of the fluorescence emission for poly(*N*-vinylcarbazole)-triethylborane complex (left; before F⁻ addition) and poly(*N*-vinylcarbazole)/borate mixture (right; after F⁻ addition).

3.2. Preparation of poly(*N*-vinylcarbazole)-triethylborane complex

Poly(*N*-vinylcarbazole)-triethylborane complex was typically prepared as follows. To a THF solution (2 ml) of poly(*N*-vinylcarbazole) (386 mg, 2.0 unit mmol), 2.0 ml of 1.0 M THF solution of triethylborane (Aldrich; 2.0 mmol) was added at room temperature, and the reaction mixture was stirred for 12 h. After the solvent was removed under reduced pressure, a white gum was obtained (550 mg, 1.90 unit mmol).

¹H NMR (CDCl₃, δ, ppm) 1.17–1.27 (9H, BCH₂CH₃), 1.83–1.88 (8H, CH₂CHN, BCH₂CH₃), 3.72–3.74 (1H, CH₂CHN), 6.01–7.98 (8H, Ar–H).

¹¹B NMR(CDCl₃, δ, ppm) 18.4.

Poly(*N*-vinylcarbazole)-tributylborane complex and poly(*N*-vinylcarbazole)-triphenylborane complex were prepared similarly to the case of poly(*N*-vinylcarbazole)-triethylborane complex by using tributylborane or triphenylborane instead of triethylborane.

Poly(*N*-vinylcarbazole)-tributylborane complex; 386 mg (2.0 unit mmol) of poly(*N*-vinylcarbazole); 2.0 ml of 1.0 M THF solution of tributylborane (2.0 mmol).

¹H NMR (CDCl₃, δ, ppm) 0.86–0.95 (9H, BCH₂CH₂CH₂CH₃), 1.32–1.60 (18H, BCH₂CH₂CH₂CH₃), 1.83–1.94 (2H, CH₂CHN), 3.75–3.82 (1H, CH₂CHN), 6.00–8.10 (8H, Ar–H).

¹¹B NMR(CDCl₃, δ, ppm) 18.9.

Poly(*N*-vinylcarbazole)-triphenylborane complex; 193 mg (1.0 unit mmol) of poly(*N*-vinylcarbazole); 240 mg (1.0 mmol) of triphenylborane.

¹H NMR (CDCl₃, δ, ppm) 1.80–1.87 (2H, CH₂CHN), 3.72–3.77 (1H, CH₂CHN), 6.91–8.09 (23H, Ar–H).

¹¹B NMR(CDCl₃, δ, ppm) 29.5.

3.3. Reaction of poly(*N*-vinylcarbazole)-borane complex with tetrabutylammonium fluoride (TBAF)

The reaction of PVCz–borane complex with TBAF was typically carried out as follows. To a THF solution (2.0 ml) of PVCz–borane complex (2.0 unit mmol), equimolar amount of TBAF (1.0 M in THF; 2.0 ml, 2.0 mmol) was added at room temperature, and the reaction mixture was stirred for 24 h. After the removal of the sol-

vent under a reduced pressure, the residue was dissolved in designated solvents for spectroscopic analysis (UV–Vis absorption, fluorescence emission and NMR spectroscopy).

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