

## Synthesis of novel poly(pyrazabole)s with electron-withdrawing structure in their main chain

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### Summary

Novel organoboron polymers containing pyrazabole and electron withdrawing moiety in the main chain were prepared by Heck-Sonogashira coupling. The coupling reaction between various diyne monomers and pyrazabole derivatives gave the corresponding polymers in good yields. The optical properties of the obtained polymers were investigated by UV-vis absorption and fluorescence spectroscopy. The relation between the electron density on the boron atoms and the optical properties of the corresponding polymers was also studied.

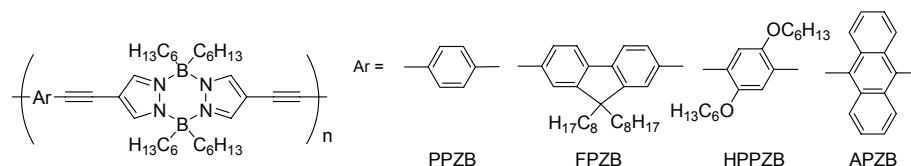
### Introduction

We have synthesized a wide variety of organoboron polymers including boron atoms in the main chain by means of hydroboration polymerization. These polymers exhibited various interesting properties due to the high electron affinity of boron atoms; strong fluorescence emission, n-type electronic conductivity and third-order nonlinear optical properties, etc [1]. Because of their unique properties, they are expected as a novel type of optical and electronic materials.

On the other hand, pyrazaboles are known as a class of boron heterocycles. Since its first synthesis [2] in 1967, a number of pyrazaboles have been prepared and characterized; but their structures and properties are not fully understood. Pyrazaboles are so stable that the derivatives containing various functional groups are readily available via usual organic reactions. Several applications of pyrazaboles have been performed recently such as possible building blocks for discotic liquid crystals [3] or good bridges for *ansa*-ferrocenes to form the active container molecule for supramolecular applications [4].

Previously, we have synthesized the poly(*p*-phenylene-ethynylene) derivatives containing the pyrazabole structures as a novel type of organoboron polymers [5] (Figure 1). These polymers were obtained in high molecular weights and good yields. Furthermore, they were highly stable against air and moisture, and showed blue fluorescent emission with high quantum emission yields. Their emission properties were attractive as a novel class of optical materials; however the mechanism of the

emission was not fully understood. As a result of UV-vis absorption measurements of the polymers and the model compounds, a slight extension of  $\pi$ -conjugation via the six-membered ring structure of boron and nitrogen was suggested in these polymers. Moreover, the similar emission spectra were observed independent of the polymer structures. From these results, the pyrazabole structures seemed to play a significant role in the emission properties. In the present paper, we synthesized novel organoboron polymers containing electron withdrawing structures and the pyrazaboles, then examined the electron state on the six-membered pyrazabole structure. The pyrazaboles normally act as an electron acceptor, thus the combination with the electron withdrawing moieties will be expected to give a great change toward their properties. The influence on the emission properties of the pyrazabole structure in these poly(pyrazabole)s was also investigated.

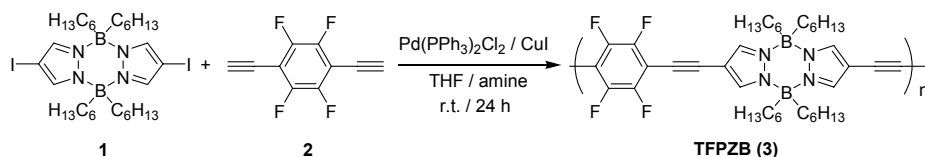


**Figure 1.** Structure of poly(pyrazabole)s

## Results and Discussion

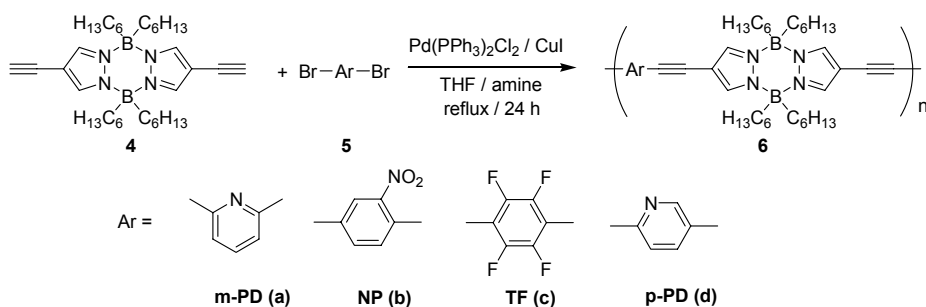
### Synthesis of polymers

As electron-withdrawing structures, we tried to incorporate tetrafluorophenylene, pyridinediyl and nitrophenylene groups into the polymer backbone. We applied the Heck-Sonogashira coupling reaction to prepare polymers. Generally, the reactivity of halogen atoms attached to an electron withdrawing aromatic moiety is not sufficient for preparing polymers with high molecular weights [6]. Thus diyne derivatives of the electron-withdrawing moiety were preferred in such a case. At first, we tried the coupling polymerization between 1,4-diethynyltetrafluorobenzene and 2,6-diiodopyrazabole (Scheme 1).



**Scheme 1.** Synthesis of TFPZB (3)

However the molecular weight of the TFPZB (3) was relatively low contrary to our anticipation. Then we applied the polymerization with inverted combination of monomers as described in Scheme 2, which gave *m*-PDPZB (6a), NPPZB (6b), TFPZB (6c) and *p*-PDPZB (6d) with high molecular weights. We investigated the reason why the molecular weight of the TFPZB (3) was low compared to others. From the comparison of the elemental analyses, the result of the TFPZB (6c) corresponded to the calculated data, however that of TFPZB (3) was relatively



**Scheme 2.** Polymerization of diethynylpyrazabole (**4**) with various monomers (**5**)

mismatched. Furthermore, the <sup>11</sup>B-NMR spectra of the TFPZB (**3**) showed the peak in lower magnetic field than that of the TFPZB (**6c**). This indicates the lower electron density on boron atoms caused by the electron withdrawing property of tetrafluorobenzene units, that is, the TFPZB (**3**) contains unexpectedly larger amount of tetrafluorobenzene moieties than pyrazabole units. In fact, diiodopyrazabole (**1**) was not reactive either, so that the homo coupling of monomer (**2**) was preferred in Scheme 1. The polymerization results are summarized in Table 1.

**Table 1.** Polymerization results

Polymer	$M_n^a$	$M_w^a$	$M_w/M_n^a$	Yield (%) <sup>b</sup>
TFPZB ( <b>3</b> )	2,800	8,900	3.17	50
<i>m</i> -PDPZB ( <b>6a</b> )	11,400	21,300	1.87	80
NPPZB ( <b>6b</b> )	6,400	12,000	1.92	68
TFPZB ( <b>6c</b> )	11,400	41,300	3.62	84
<i>p</i> -PDPZB ( <b>6d</b> )	8,600	23,500	2.73	83

<sup>a</sup> Measured by GPC (THF). Polystyrene standards.

<sup>b</sup> Isolated yields after reprecipitation into MeOH.

### Optical properties

The optical properties of the obtained polymers were investigated through UV-vis absorption and fluorescence emission spectra measurements (Table 2). The absorption peaks of *p*-PDPZB (**6d**) lied in longer wavelength region compared to that of *m*-PDPZB (**6a**). This observation can be rationalized by the favored structure of *p*-PDPZB (**6d**) for  $\pi$ -conjugation, which has a straight main chain due to the para-substituted pyridine moiety against the meta-configuration of *m*-PDPZB (**6a**). TFPZB (**3**) showed the similar absorption and emission peaks as TFPZB (**6c**), however had the additional peaks at 393 and 523 nm in the emission spectra. These peaks should be attributed to the irregular structure as described above, that led to the lower fluorescence quantum yields of TFPZB (**3**) compared to that of TFPZB (**6c**). On the other hand, NPPZB (**6b**) showed no fluorescence emission peaks. This phenomenon was also observed in some chromophores [7] and poly(*p*-phenyleneethynylene) derivatives [8] containing nitro groups. Thus, it was understood that the fluorescence quenching was caused by the incorporation of the nitro groups in the case of NPPZB (**6b**).

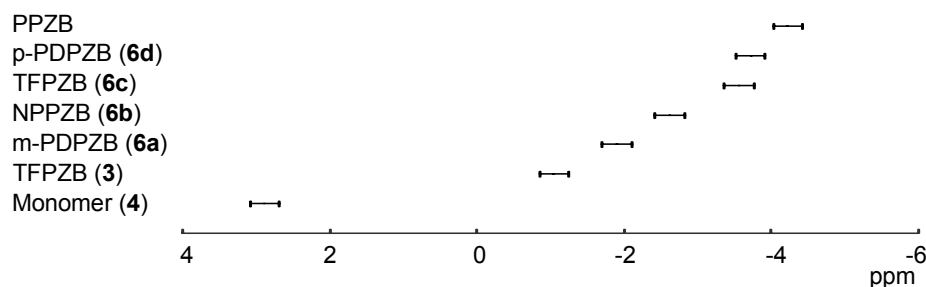
**Table 2.** UV-vis absorption and fluorescence properties <sup>a</sup>

Polymer	$\lambda_{\max}$ (nm)	Ex (nm) <sup>b</sup>	FL (nm) <sup>c</sup>	$\Phi_D$ <sup>d</sup>
TFPZB ( <b>3</b> )	343	344	350, 371, 393, 523	0.10
<i>m</i> -PDPZB ( <b>6a</b> )	244, 286, 315	332	350	0.11
NPPZB ( <b>6b</b> )	277, 317	- <sup>e</sup>	- <sup>e</sup>	- <sup>e</sup>
TFPZB ( <b>6c</b> )	295, 313, 342	342	350, 371	0.23
<i>p</i> -PDPZB ( <b>6d</b> )	320	331	353, 384	0.63

<sup>a</sup> Measured in chloroform at room temperature. <sup>b</sup> Excited wavelength. <sup>c</sup> Fluorescence maximum wavelength. <sup>d</sup> Fluorescence quantum yields, *p*-terphenyl standards. <sup>e</sup> Polymer (**6b**) shows no fluorescence emission.

### <sup>11</sup>B-NMR study of polymers

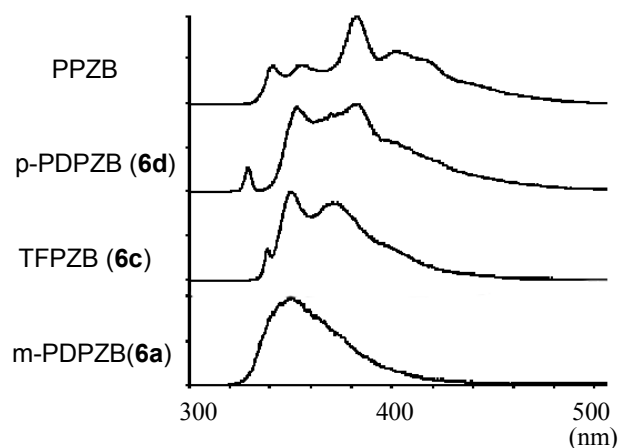
As previously reported, the boron atoms of pyrazabole relayed the electrons on the pyrazole rings weakly, thus the electron density of the boron atoms was affected by the electron state of the polymer main chain. The chemical shifts in <sup>11</sup>B-NMR measurements reflected the trend of the obtained polymers. In Figure 2, the data are described with error bars, because the peaks in <sup>11</sup>B-NMR measurements had inaccuracy in some extent due to the low sensitivity to the boron isotopes in polymers.

**Figure 2.** <sup>11</sup>B-NMR chemical shifts of prepared polymers and monomer (**4**)

Compared to PPZB (illustrated in Figure 1), which has no electron withdrawing structure, higher chemical shifts were observed in the obtained polymers. Thus it was suggested that the electron withdrawing structures reduced the electron density on the boron atoms effectively. However, the chemical shift of the monomer (**4**) was highest in this legend, so that the electron density on the boron atoms in polymer state would be higher than that in monomeric state. To say precisely, pyrazaboles have strong electron affinity even against the electron withdrawing structures.

The fluorescence spectra of some polymers are shown in the order of the <sup>11</sup>B-NMR chemical shifts (Figure 3). As decreasing the electron density on the boron atoms, the emission peaks moved to shorter wavelengths. Furthermore, the number of peaks and shoulders was reduced in this direction. The spectrum of PPZB should be regarded to reflect the electron transition on the pyrazabole structure because the electron density on the moiety was highest in these polymers. However in *m*-PDPZB (**6a**), the density was relatively low and the effect of the pyrazabole moiety would not be shown

significantly in the spectrum. Thus, the multiple peaks on the spectra suggested the typical emission of the pyrazabole moiety. The fluorescence quantum yields were also related to the electron state on the pyrazabole. As shown in Table 2, the quantum yield was highest in the *p*-PDPZB (**6d**) which had the high electron density, and lowest in *m*-PDPZB (**6a**). This result indicates that the pyrazabole structure is significant for the emission properties.



**Figure 3.** Fluorescence emission spectra of polymers, aligned in the order of  $^{11}\text{B}$ -NMR chemical shifts from top to bottom

## Conclusion

Novel organoboron polymers containing pyrazabole and electron withdrawing structure were prepared. The obtained polymers exhibited blue to near-ultraviolet emission. By incorporating the electron withdrawing structure to the main chain, the electron density on the boron atom was reduced, and their emission wavelengths and fluorescence quantum yields were decreased accordingly. The emission spectra suggested the strong relation between the pyrazabole and their emission properties. Furthermore, they were highly stable and exhibited good film formability. So they are expected as new optical materials which have near-ultraviolet emissions.

## Experimental

**Materials and Instrument:** Tetrahydrofuran (THF) and diisopropylamine were distilled before use.  $^1\text{H}$ - and  $^{11}\text{B}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with polystyrene standards. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. 4,4,8,8-Tetrahexyl-2,6-diiodopyrazabole (**1**) [5], 1,4-diethynyltetrafluorobenzene (**2**) [9] and 2,6-diethynyl-4,4,8,8-tetrahexylpyrazabole (**4**) [5] were prepared according to the literature. Other reagents were commercially available and purified before use. All reactions were performed under nitrogen atmosphere.

**TFPZB (3).** To a mixture of 2,6-diiodopyrazabole (**1**) (0.2245 g, 0.30 mmol), 1,4-diethynyltetrafluorobenzene (**2**) (0.059 g, 0.30 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.005 g, 0.008 mmol), CuI (0.001 g, 0.008 mmol) and 10 ml of THF, 5 ml of diisopropylamine was added at room temperature. After refluxing for 24 h, the solvents were removed in vacuo. The residue was poured into *t*-butyl methyl ether and the ammonium salt was removed from the solution by filtration. The reddish product (0.1493 g, 50%) was reprecipitated from methanol and dried. NMR data (solution in CDCl<sub>3</sub>): δ (<sup>1</sup>H, ppm) = 7.78 (4H, Pz), 1.17-0.69 (52H, hexyl); δ (<sup>13</sup>C, ppm) = -1.05. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub>: C, 8.17; H, 69.58; N, 8.11. Found: C, 5.96; H, 56.82; N, 5.42.

***m*-PDPZB (6a).** The reaction was carried out following the procedure described above. The polymerization between 0.071 g (0.30 mmol) of 2,6-dibromopyridine and 0.23 g (0.30 mmol) of the monomer (**4**) gave the corresponding polymer (**6a**) (0.1487 g, 80%) as a yellow-white solid. NMR data (solution in CDCl<sub>3</sub>): δ (<sup>1</sup>H, ppm) = 7.74 (4H, Pz), 7.63 (1H, Py), 7.38 (2H, Py), 1.17-0.69 (52H, hexyl); δ (<sup>13</sup>C, ppm) = -1.91.

**NPPZB (6b).** The reaction of 0.084 g (0.30 mmol) of 2,5-dibromonitrobenzene and 0.1633 g (0.30 mmol) of the monomer (**4**) gave the polymer (**6b**) in 68 % yield (0.1395 g) as a greened white solid. NMR data (solution in CDCl<sub>3</sub>): δ (<sup>1</sup>H, ppm) = 8.26 (1H, Ar), 7.82 (1H, Ar), 7.70 (4H, Pz), 7.59 (1H, Ar), 1.17-0.69 (52H, hexyl); δ (<sup>13</sup>C, ppm) = -2.62.

**TFPZB (6c).** The reaction of 0.1232 g (0.40 mmol) of 1,4-dibromotetrafluorobenzene and 0.2177 g (0.40 mmol) of the monomer (**4**) was performed. The yellow product (**6c**) was prepared in 84 % yield (0.1731 g). NMR data (solution in CDCl<sub>3</sub>): δ (<sup>1</sup>H, ppm) = 7.78 (4H, Pz), 1.17-0.69 (52H, hexyl); δ (<sup>13</sup>C, ppm) = -3.56. Anal. Calcd for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub>: C, 8.17; H, 69.58; N, 8.11. Found: C, 8.38; H, 65.46; N, 7.94.

***p*-PDPZB (6d).** The reaction of 0.071 g (0.30 mmol) of 2,5-dibromopyridine and 0.1633 g (0.30 mmol) of the monomer (**4**) gave the polymer (**6d**) in 83 % yield (0.1546 g) as a white solid. NMR data (solution in CDCl<sub>3</sub>): δ (<sup>1</sup>H, ppm) = 8.69 (1H, Py), 7.75 (4H, Pz), 7.41 (1H, Py), 7.30 (1H, Py), 1.17-0.69 (52H, hexyl); δ (<sup>13</sup>C, ppm) = -3.72.

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