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π-Conjugated Poly(cyclodiborazane)s with Intramolecular Charge Transferred Structure

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Much efforts have been paid so far for the synthesis of π-electron-deficient n-type π-conjugated polymers[1] in search for appropriate electron transport materials in light-emitting diodes and organic negative electrodes in energy storage systems. The organoboron π-conjugated polymers might be one of the good candidates for such materials. Recently, we have reported synthesis of a series of π-conjugated organoboron polymers via the empty p-orbital of the boron atom by means of hydroboration polymerization[2] or polycondensation.[3] These polymers exhibited unique characteristics such as intense fluorescense emission, excellent third-order nonlinear optical behavior, and n-type electrochemical activity.

On the other hand, poly(cyclodiborazane)[4] is a new class of highly inorganic polymeric materials[5] that exhibit reasonable stability toward air and moisture. Hydroboration polymerization of aromatic dicyano compounds with a *tert*-butylborane−trimethylamine complex or mesitylborane gives soluble poly(cyclodiborazane)s in good yields.

Although fully aromatic poly(cyclodiborazane)s should be also regarded as π-conjugated organoboron polymers via the vacant p-orbital of the boron atom, no significant extension of π-conjugation length was observed in the previously reported systems.[6] However, incorporation of charge transferred structure in their backbone might bring about a dramatic change in their electronic structure. This paper describes hydroboration polymerization of dicyano compounds with intramolecular charge transferred (ICT) structure to afford π-conjugated poly(cyclodiborazane)s. The polymers obtained were highly fluorescent and showed dramatically bathochromic shifted absorption edges in comparison with those for model compounds.

First of all, hydroboration polymerization between 1,4-dioctoxy-2,5-dicyanobenzene (**1a**) and mesitylborane (**2**) was examined. To a THF solution of **1a**, a slightly excess amount of **2** in THF was added dropwise at room temperature. During the addition, the reaction mixture turned to a fluorescent yellow-green solution. After stirring the mixture overnight, evaporation of the solvent gave a yellow-green gum quantitatively. After the reprecipitation into MeOH, the corresponding polymer (**3a**) was obtained as a yellow powder in 50% yield. From the gel permeation chromatographic analysis (THF, PSt standards), the number-average molecular weight of **3a** was estimated to be 5800. **3a** was very soluble in common organic solvents such as THF, chloroform, benzene, *n*-hexane, and so on. Instead of **1a**, 2,5-dicyanothiophene (**1b**) also gave the corresponding polycyclodiborazane (**3b**, M_n 4700) in a good yield (89%) (Table 1) after washing with *n*-hexane.

The structures of these polymers were supported by ^{1}H NMR, ^{11}B NMR, and IR spectra. For example, in the ^{1}H NMR spectrum of **3a**, the peaks corresponding to the mesityl group were observed at 6.64−7.01 and 2.13−2.63 ppm. The peak at 8.39 ppm is assignable to imino proton (C*H*=N). The ^{11}B NMR spectrum of **3a** shows the main peak at 0.86 ppm, which indicates the formation of cyclodiborazane units. (The smaller peak at 31 ppm is ascribed for monomeric iminoborane at the end group.) From the IR spectrum of **3a**, sharp absorption peaks due to B−H and C=N stretching were observed at 2369 and 1637 cm^{-1}, respectively.

Scheme 1

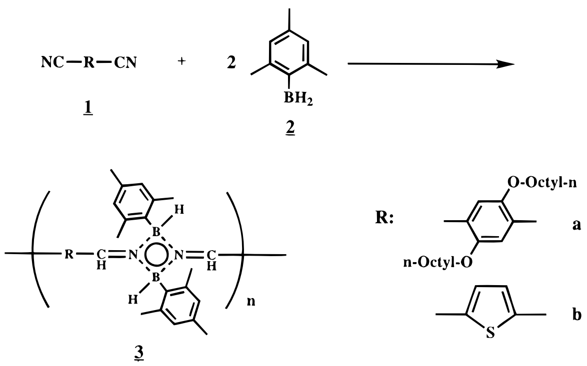
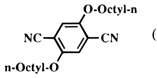
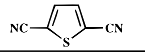


Table 1. Hydroboration Polymerization between 1 and 2[a]

Run	1		2/1	*Mw* b)	*Mn* b)	*Mw/Mn* b)	Yield (%) c)
1		(1a)	2.02	7900	5800	1.4	50
2		(1b)	2.15	9400	4700	2.0	89

[a] The reactions were carried out in THF at room temperature. [b] GPC (THF), polystyrene standards. [c] Isolated yields after reprecipitation into MeOH (**1a**) or washing with *n*-hexane (**1b**).

Table 2. Optical Data of Dicyano Compounds (1), Poly(cyclodiborazane)s (3), and Their Model Compounds (4)

run	compd or polymer	UV λ_{max}[a]	ϵ[a]	UV λ_{edge}[a]	PL λ_{max}[b]
1	**1a**	359	4310	384	389
2	**3a**	381	21000	461	463
3	**4a**	318	4980	351	470
4	**1b**	331	2580	372	393
5	**3b**	364	14000	451	473
6	**4b**	277	22000	391	467

[a] In CHCl$_3$, at room temperature. [b] In CHCl$_3$, at room temperature.

The optical data of donor−acceptor poly(cyclodiborazane)s are summarized in Table 2. The UV−vis spectrum of **3a** exhibited the absorption maximum at 381 nm, which indicates the presence of some intramolecular charge-transfer interaction or interunit conjugation along the main chain of the polymer. Especially, absorption edges of the peaks for **3a,b** were dramatically bathochromic shifted in comparison with that for the dicyano monomers (**1a,b**) or the model compounds (**4a,b**). This suggests interunit π-conjugation should be also prevailing in the backbone. The polymers obtained (**3a**,**b**) exhibited intense blue-green light emissions upon irradiation with ultraviolet or near-ultraviolet light. When a dilute chloroform solution of **3a** was irradiated at 400 nm, the fluorescence emission spectrum showed an intense emission peak in the visible blue-green region (λ_{max} 463 nm). The location of the emission maxima was

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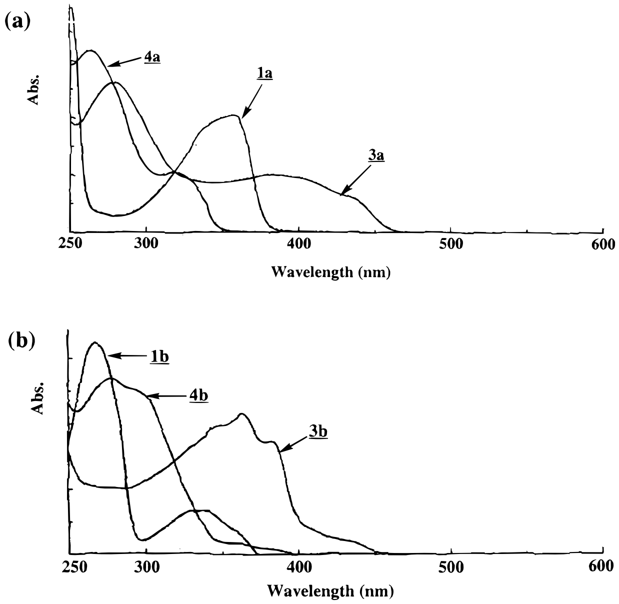


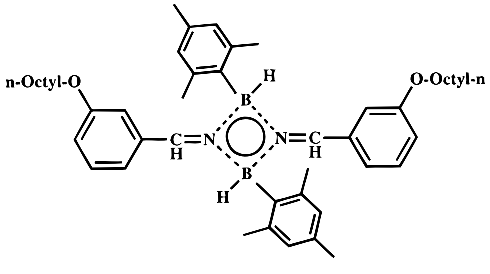
Figure 1. UV−vis absorption spectra of **1a,b** (dicyano compound), **3a,b** (polymer), and **4a,b** (model compound) in chloroform at room temperature.

Table 3. Fluorescence Emission Maxima of 3a in Various Organic Solvents

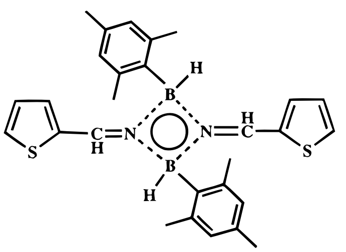
solvent	DMF	CH_2Cl_2	$CHCl_3$	CH_3CO_2Et	THF	Et_2O	*n*-hexane
λ_{max}	475	467	463	460	465	456	452

[a] At room temperature. Excitation wavelength at 400 nm.

found to be dependent on the kind of solvents employed (Table 3). For example, the emission in *n*-hexane solution led to the observation of a slightly blue-shifted emission peak (λ_{max} 452 nm). On the other hand, in a polar solvent, DMF, a red-shifted emission maximum was observed at 475 nm. However, the extent of these solvent effects was not strictly in the order of polarity of solvents and possibly includes strength of solvation as another factor, which might change the chain conformation and affect the intramolecular energy transfer process, even though the polarity of solvents and the resulting changes in the level of the excited states seem to be most predominant factor in these observations.



4a



4b

The air stabilities of these polymers were investigated by an air bubbling experiment. A stream of air was bubbled in THF solution of **3a** or **3b**, and the changes of the molecular weights were monitored by gel permeation chromatographic analysis (GPC) for 24 h. In both cases, no significant change in the GPC curve was observed during the measurements. The stabilities of **3a** and **3b** toward moisture were also examined by adding water to these polymers and stirring the resulting mixtures for 24 h. After these treatments, similarly, the GPC curves did not change compared with those for the starting polymers.

In summary, extended π-conjugation through the cyclodiborazane unit was observed in the fully aromatic poly(cyclodiborazane)s having intramolecular charge transferred (ICT) structure. The fairly bathochromic shifted absorption edges of the obtained polymers relative to those for model compounds indicate that intraunit π-conjugation in addition to charge transferred structure should be concerned with the specific electronic state of the present system.

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Supporting Information Available: Experimental details for the synthesis of **3a,b** and their characterization data (^{1}H NMR, ^{11}B NMR, IR, and fluorescence emission spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For example: (a) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (b) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930. (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.

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(6) The UV−vis spectra of poly(cyclodiborazane)s prepared from 1,4-dicyanobenzene[4] or 9,10-dicyanoanthracene[7] did not show particularly red-shifted absorption maxima or edges in comparison with the corresponding dicyano monomers. However, the latter showed only one broad band at 406 nm (in $CHCl_3$, at room temperature), while DCA had three sharp bands at 377, 402, and 426 nm. This change of band structure might be due to some conjugative interaction.

(7) Matsumi, N.; Naka, K.; Chujo, Y. *Macromolecules* **1998**, *31*, 8047.

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