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Comparison of UV–Vis Changes Observed in Deprotonation of 2-Heptylbenzimidazole, 2-Heptyl-4,7-diphenylbenzimidazole, and Poly(2-heptylbenzimidazole-4,7-diyl)

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Shifts of the UV–vis peak caused by deprotonation of 2-heptylbenzimidazole and sterically strained 2-heptyl-4,7-diphenyl-benzimidazole and poly(2-heptylbenzimidazole-4,7-diyl) (**P[4,7-Bim(Hep)]**) are discussed. The π–π^* absorption band of the strained molecules showed a large shift to a longer wavelength on deprotonation with NaOH. **P[4,7-Bim(Hep)]** showed a new absorption peak at about 400 nm.

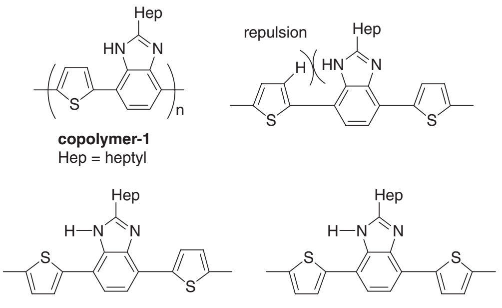
We previously reported synthesis of a π-conjugated alternative copolymer of thiophene and 2-heptylbenzimidazole, **copolymer-1**.[1]

This **copolymer-1** is considered to have the following triads, which receive H–H and/or H–S repulsion to distort the coplanar structure (Chart 1).

Deprotonation of the N–H group in the polymer is expected to release the repulsion. Actually, the deprotonation of **copolymer-1** by NaOH brought a large shift of the π–π^* absorption band to a longer wavelength from 458 nm to 550 nm.[1]

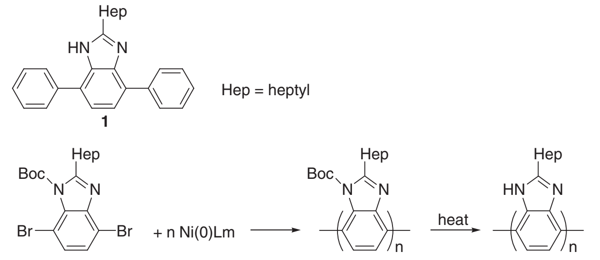
In order to study the effect of such release of steric repulsion in more detail, we have prepared the following trimeric compound, **1**, and poly(2-heptylbenzimidazole-4,7-diyl), **P[4,7-Bim(Hep)]**, and we herein report UV–vis results for their deprotonation reactions (Scheme 1).

P[4,7-Bim(Hep)] was prepared according to the organometallic polycondensation,[2,3] it had a number-averaged molecular weight of 3000, as determined by gel permeation chromatography.



copolymer-1
Hep = heptyl

Chart 1.



P[4,7-Bim(Hep)]

Boc = *t*-butoxycarbonyl,
Ni(0)L$_m$ = a mixture of bis(1,5-cyclooctadiene)nickel(0),
Ni(cod)$_2$, and 2,2'-bipyridyl, bpy

Scheme 1.

Figure 1 shows changes of the UV–vis spectra of 2-heptylbenzimidazole, **1**, and **P[4,7-Bim(Hep)]** on the deprotonation with NaOH. The deprotonation of 2-heptylbenzimidazole causes only a small shift of the absorption peak by 10 nm to a longer wavelength, in accord with reported data of 2-methylbenzimidazole.[4] On the other hand, **1** receives a large bathochromic shift of the UV–vis peak by 36 nm on the deprotonation. Use of a stronger deprotonation reagent, NaH, brings about essentially the same UV–vis changes of 2-heptylbenzimidazole and **1**.

P[4,7-Bim(Hep)] shows a UV–vis peak at 285 nm. The peak position locates at a considerably shorter wavelength compared with that (ca. 370 nm) of poly(*p*-phenylene),[2,3,5,6] presumably due to the twisting. When it is deprotonated, the steric repulsion seems to be partly released to show a large shift by 50 nm to a longer wavelength.

At a low degree of deprotonation, only a rise of the peak at 335 nm is observed; however, further deprotonation brings about a new broad absorption band at about 400 nm. Such a new peak is not observed for **1** with a short π-conjugation length. The peak at about 400 nm may be taken as a sign that indicates generation of a polaronic or bipolaronic state, which is often generated in charged (or doped) π-conjugated polymers[5–7] (Scheme 2).

The negative charge in the side chain in **P[4,7-Bim(Hep)]** may partly penetrate into the main chain to form the polaronic or bipolaronic state; if it occurs, it gives a new example of generation of such electronic state(s) caused by the side chain ionization of π-conjugated polymer. On the other hand, many examples have been reported for generation of the polaronic or bipolaronic state by direct reduction of the main chain of the π-conjugated polymers.[5–7]

The compounds shown above were photoluminescent, and the quantum yield of **P[4,7-Bim(Hep)]** increased on the deprotonation. Table 1 summarizes the photoluminescence (PL) data.

The present results reveal the effects of the release of steric repulsion by the deprotonation in the strained π-conjugated benzimidazole compounds and suggest that charging of the side chain can generate the polaronic or bipolaronic state in the π-conjugated polymers. The quantum efficiency of PL of **P[4,7-Bim(Hep)]** increased by the deprotonation. These findings are expected to contribute to better understanding and application of π-conjugated polymers of benzimidazole.

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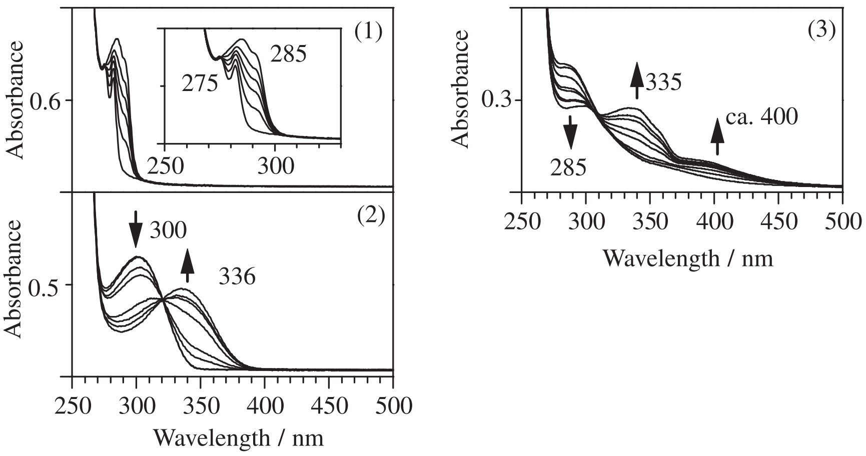
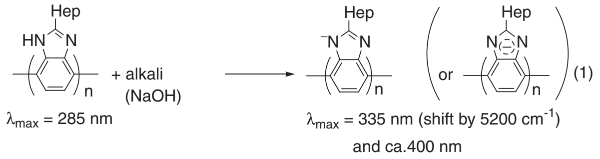


Fig. 1. Changes of UV–vis spectra of (1) 2-heptylbenzimidazole (8.6×10^{-5} M; M = 1 mol dm^{-3}), (2) **1** (1.7×10^{-5} M), and (3) **P[4,7-Bim(Hep)]** (4.3×10^{-5} M; molarity is based on the 2-heptylbenzimidazole unit). Solvent = 6:1 (v/v) mixture of DMF and MeOH. [NaOH]/10^{-4} M: for (1): a) none, b) 1.7, c) 2.6, d) 3.4, e) 4.3, f) 8.6; for (2): a) none, b) 0.14, c) 0.21, d) 0.29, e) 1.4, f) 2.1, g) 340; for (3): a) none, b) 1.3, c) 1.4, d) 1.5, e) 1.6, f) 1.7, g) 2.1, h) 43.



Scheme 2.

Table 1. Photoluminescence Data[a)]

State	2-Heptylbenzimidazole	1	P[4,7-Bim(Hep)]
Neutral	298 (0.26)	370 (0.64)	354 (0.08)
Anionic[b)]	317 (0.08)	412 (0.59)	399 (0.20)

a) Emission peaks are shown. The number in the parentheses indicates the quantum efficiency. Measured in DMF. b) At [NaOH] = 0.02 M in a 6:1 (v/v) mixture of DMF and MeOH.

Experimental

$Ni(cod)_2$ and 4,7-dibromo-2-heptylbenzimidazole (**2**) were prepared according to the literature.[8]

Synthesis of 1 and P[4,7-Bim(Hep)]. 1: To a mixture of toluene (20 cm^3) solution of **2** (0.37 g, 1.0 mmol) and $Pd(PPh_3)_4$ (1.0 mg) and an aqueous solution of sodium carbonate (4.0 cm^3, 2.0 M), was added an ethanol (10 mL) solution of phenylboronic acid (0.24 g, 2.0 mmol). After the reaction mixture was stirred at 80 °C for 16 h, hydrogen peroxide (30%) was added slowly. The mixture was stirred for 4 h and extracted with $CHCl_3$. The extract was washed with an aqueous solution of NaOH and water. The organic layer was dried over $MgSO_4$ and the solvent was removed. Purification by column chromatography (SiO_2–$CHCl_3$) yielded **1** as a white solid. Yield 70%. Found: C, 84.42; H, 7.74; N, 7.55%. Calcd for $C_{26}H_{28}N_2$: C, 84.74; H, 7.66; N, 7.60%. ^{1}H NMR ($CDCl_3$) δ 9.08 (br, 1H, NH), 8.04 (s, 2H), 7.65 (s, 4H), 7.35 (br, 4H), 2.92 (t, 2H), 1.82 (m, 2H), 1.58 (br, 2H), 1.29 (m, 8H), 0.88 (m, 3H).

1-*t*-Butoxycarbonyl-4,7-dibromo-2-heptylbenzimidazole (Br_2Bim(Hep)Boc): After a THF (20 cm^3) solution of 4-dimethylaminopyridine (37 mg, 0.30 mmol) and **2** (0.36 g, 1.0 mmol) was stirred for 5 min, di-*t*-butyl dicarbonate ($(Boc)_2O$) (0.26 cm^3, 1.0 mmol) was added to the solution. The reaction mixture was stirred at 80 °C for 5 h and cooled to room temperature. Removal of the solvent gave a clear solid, which was purified by column chromatography (SiO_2–$CHCl_3$) and recrystallized from hexane–$CHCl_3$ to give Br_2Bim(Hep)Boc. Yield 71%. Found: C, 48.04; H, 5.52; N, 6.07; Br, 34.00%. Calcd for $C_{19}H_{26}Br_2N_2O_2$: C, 48.12; H, 5.53; N, 5.91; Br, 33.70%. ^{1}H NMR ($CDCl_3$) δ 7.33 (t, 2H, $J = 5.9$ Hz), 3.00 (t, 2H, $J = 7.8$ Hz), 1.82 (m, 2H), 1.71 (m, 9H), 1.40 (m, 2H), 1.29 (m, 6H), 0.88 (t, 3H).

Poly(2-heptylbenzimidazole-4,7-diyl) (P[4,7-Bim(Hep)]): To a toluene solution containing $Ni(cod)_2$ (0.83 g, 3.2 mmol), 1,5-cyclooctadiene (0.35 g, 3.2 mmol), and bpy (0.47 g, 3.2 mmol), Br_2Bim(Hep)Boc (0.47 g, 1.0 mmol) was added. The reaction mixture was stirred at 60 °C for 96 h to give a black precipitate. The precipitate was washed with aqueous ammonia, and with an aqueous solution of Na_2EDTA at room temperature, and with a distilled water at 50 °C, and dried under vacuum to give Boc-polymer as a red powder. Under nitrogen atmosphere, Boc-polymer was heated at 200 °C for 1 h to give a red powder of **P[4,7-Bim(Hep)]**. Deprotection was confirmed by IR and ^{1}H NMR spectra. Total yield 32%. Found: C, 74.55; H, 8.10; N, 12.34; Br, 0%. Calcd for $(C_{14}H_{18}N_2 \cdot 0.4H_2O)_n$: C, 75.91; H, 8.55; N, 12.65%. ^{1}H NMR (DMSO-d_6) δ 12.55 (s, 1H, NH), 7.49 (s, 1H), 7.23 (s, 1H), 2.82 (s, 2H), 1.77 (m, 2H), 1.24 (m, 8H), 0.83 (s, 3H).

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