

## ORIGINAL ARTICLE

# Synthesis and fluorescent properties of conjugated co-oligomers containing maleimide and carbazole units at the main chain

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Yamamoto coupling polymerizations of 2,3-diiodo-*N*-cyclohexylmaleimide (DICHMI) with dihalide carbazole derivatives (DXRCz) (3,6-dibromo-*N*-methylcarbazole (3,6-DBrMCz), 3,6-diiodo-*N*-hexylcarbazole (3,6-DIHCz) and 2,7-dibromo-*N*-hexylcarbazole (2,7-DBrHCz)) were performed using a nickel complex. The number-average molecular weights ( $M_n$ ) of poly(*N*-cyclohexylmaleimide-*co*-*N*-substituted carbazole)s (poly(CHMI-*co*-RCz)) were in the range of 600–7300, as determined by gel permeation chromatography analyses. The fluorescence emissions of the poly(CHMI-*co*-RCz) solution showed two emission maxima in the 417–426 and 581–595 nm regions. The fluorescence peaks of co-oligomers at long wavelengths (581–595 nm) were attributable to the conjugated neighboring CHMI-RCz units of polymer main chains. The intensities of fluorescence emissions were significantly affected by the polarity of organic solvents such as tetrahydrofuran and *N,N*-dimethylformamide. The solvatochromic fluorescence phenomenon may be attributable to the twisting of CHMI-RCz bonds in an excited state in polar solvents.

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## INTRODUCTION

$\pi$ -Conjugated polymers may be applied to new organic electronic materials such as organic light-emitting diodes,<sup>1–10</sup> organic field-effect transistors,<sup>11,12</sup> photovoltaic cells<sup>13–16</sup> and biosensors.<sup>17–21</sup> The molecular design of monomeric units is very important because the efficiency of devices is generally affected by the purity, structure and molecular arrangement of the conjugated polymer. In various types of conjugated polymers, carbazole derivatives are known for a conjugate unit that has interesting photo and electric properties, such as photoconductivity and photorefractivity, which show good workability and high emission ability in the solid state.<sup>22,23</sup> Recently, conjugated polymers containing carbazolene units in the main chain have been widely investigated; the properties of such polymers are changed by the substitution positions of a carbazolene unit. Poly(3,6-carbazole) and poly(2,7-carbazole) derivatives can easily form homogeneous layers. Poly(2,7-carbazole) derivatives with 2,7-substituted carbazole have decreased bandgap energy because of their rod-like structure. Thus, poly(2,7-carbazole) is expected to be useful for hole transportation materials.<sup>24–27</sup>

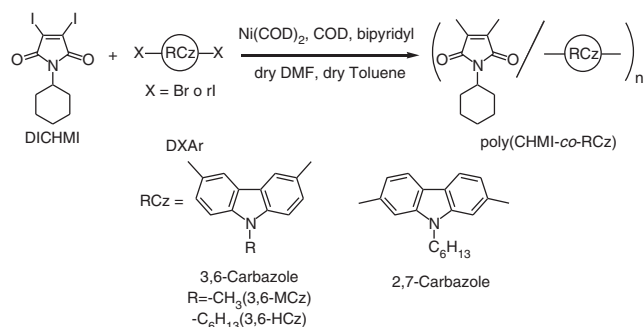
In addition, the copolymerization of carbazole derivatives with good acceptor molecules such as quinoxaline and benzothiadiazole

was reported.<sup>28,29</sup> These conjugated copolymers have a donor–acceptor unit and exhibit very interesting electronic and emission properties because the bandgap was adjustable by different types of molecules. Furthermore, carbazole copolymers are designed by alternative or random polymerization. In contrast with alternative copolymers, random copolymers can induce various feed ratios of an acceptor unit over a wide range. Therefore, the design of the random copolymer is able to change the bandgap of the copolymer.<sup>30,31</sup> In addition, the introduction of an acceptor unit can improve the charge transport properties of the random copolymer, and this copolymer is suitable for applications in multilayer polymer light-emitting diodes, as reported previously.<sup>32</sup> However, these acceptor molecules have some problems, such as the high cost of the starting materials and the multistep composition process.

However, maleimide is an imide ring compound that can be obtained from affordable maleic anhydride and easily introduce various functional groups to the *N*-position.<sup>33–35</sup> Maleimide, a cyclic olefin monomer, is considered to be *cis*-olefin and consists of a repetition unit of the *cis*-configuration, similar to polyacetylene, which is common in organic electronic device materials. Maleimide derivatives show properties of *n*-type organic semiconductor

materials such as phthalimide, naphthylimide and pyreneimide for an electron-deficient heterocyclic ring.<sup>36–39</sup> For example, Chen and co-workers<sup>40</sup> reported alternating copolymers obtained from *N*-substituted 2,3-diphenylmaleimides and the boronate of fluorene or bithiophene derivatives. The copolymer containing maleimide units showed electroluminescence emission of orange to red in a thin film. In addition, Cola and co-workers<sup>41</sup> report the ability of fluorescence sensing a zinc ion by the maleimide derivative. The results were the first report that maleimide copolymers exhibited photoluminescence (PL) and electroluminescence spectra at long wavelengths and that the maleimide comonomer had an important role as an acceptor molecule such as benzoselenadiazole and naphthoselenadiazole. Some articles relevant to the polymer of *N*-substituted-2,3-diarylmaleimide are reported, but there are few reports of copolymers in which maleimide is connected directly.<sup>42–44</sup> Using maleimide as an acceptor molecule, a low-bandgap-conjugated polymer for an organic semiconductor may be inexpensively and easily obtained. Copolymers or homopolymers of maleimide and its model compounds using various functional groups on the side chain of the maleimide moiety were reported previously.<sup>45–47</sup> A series of 1,4-phenylene- or 2,5-thienylene-based copolymers containing *N*-substituted maleimide derivatives fluoresced in a yellow to blue color in a tetrahydrofuran (THF) solution when exposed to ultraviolet light of wavelength 352 nm. It was found that the PL and electronic state of maleimide copolymers were controlled by donor molecules and *N*-substituents. The authors thought that synthesis of maleimide copolymers with donor molecules other than phenylene and thienylene groups was necessary to investigate the acceptor effects of maleimide.

In this paper, we report the Yamamoto coupling polymerization of 2,3-diiodo-*N*-cyclohexylmaleimide (DICHMI) as an acceptor moiety and dihalide carbazole consisting of 3,6 and 2,7 linking as a donor moiety and their polymerizabilities in Scheme 1. The fluorescence properties of the obtained co-oligomers are investigated. Furthermore, the authors prepare 2,3-bis(*N*-hexylcarbazol-3-yl)-*N*-cyclohexylmaleimide from DICHMI and *N*-hexylcarbazol-3-ylboronic acid as model-conjugated co-oligomers containing CHMI and RCz units. The relationship between the fluorescence and structure of a conjugated co-oligomer is investigated by a detailed comparison of model compounds.



**Scheme 1** Yamamoto coupling polymerization of DICHMI with carbazole derivatives.

## EXPERIMENTAL PROCEDURE

### Measurements

<sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA500 (JEOL, Tokyo, Japan) using tetramethylsilane (TMS) (<sup>1</sup>H NMR (proton NMR spectroscopy),  $\delta$  0.00) or CDCl<sub>3</sub> (<sup>13</sup>C NMR,  $\delta$

77.0) as internal reference peaks at room temperature at the Collaborative Center for Engineering Research Equipment, Faculty of Engineering in Yamaguchi University (Yamaguchi, Japan). Splitting patterns are designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet) and *br* (broad). Number-average molecular weights ( $M_n$ ) and molecular weight distributions ( $M_w/M_n$ ) of polymers were obtained with gel permeation chromatography (GPC) on a CROMATOPAC C-R7Ae plus (Shimadzu Corporation, Kyoto, Japan) (LC-10AS, CTO-2A, SPD-10A, JASCO OR-990) equipped with polystyrene gel columns (HSG-40G, HSG-20G, HSG-15G, HSG-10G), using THF as an eluent at a flow rate of 1.0 ml min<sup>-1</sup>, and calibrated by a polystyrene standard at 50 °C. The ultraviolet-visible (UV-vis) spectra were recorded on a UV-1650PC (Shimadzu Corporation). The PL spectra were recorded on a FP-6300 (JASCO Corporation, Tokyo, Japan) spectrophotometer. High-resolution mass spectra measurements (time of flight-mass spectrometer, LCT Premier XE; Waters Corporation, Milford, MA, USA) on a UPLC:ACQUITY Ultra-Performance LC (Waters Corporation) were conducted at the Collaborative Center for Engineering Research Equipment, Faculty of Engineering, Yamaguchi University.

### Materials

All chemicals were used without any further purification. Carbazole, 1,4-dibromo-2-nitrobenzene, triisopropyl borate and 1,5-cyclooctadiene (1,5-COD) were purchased from Tokyo Chemical Industry. Celite 545 was available from Aldrich (St Louis, MO, USA). Potassium iodide, potassium iodate, *N*-bromosuccinimide (NBS), pyridine and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Sodium thiosulfate 5-hydrate, potassium carbonate, copper powder, tin powder and 2,2'-bipyridyl were available from Kishida Reagents Chemicals (Osaka, Japan). Bromine, sodium hydride, *n*-hexyl bromide, tetrakis(triphenylphosphine)platinum (0) and anhydrous magnesium sulfate were purchased from Nakalai Tesque (Kyoto, Japan). Iodomethane, bis(1,5-COD) nickel (0), sodium sulfate and *n*-butyllithium in *n*-hexane solution (*n*-BuLi) were purchased from Kanto Chemical (Tokyo, Japan). Sodium iodide was purchased from Ishizu Seiyaku Ltd. (Osaka, Japan). *N*-cyclohexylmaleimide was offered by NOF Corporation (Tokyo, Japan). *n*-Hexane, ethyl acetate, tetrahydrofuran, *N,N*-dimethylformamide, CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were dried according to the standard procedure and distilled under nitrogen. Analytical thin-layer chromatography (TLC) was performed with Merck silica gel plate 60F<sub>254</sub>. Column chromatography was performed with silica gel 60 (0.063–0.200 mm; Merck, Gibbstown, NJ, USA).

DICHMI,<sup>45,48</sup> 3,6-dibromo-*N*-methylcarbazole (3,6-DBrMCz),<sup>49</sup> 3,6-diiodo-*N*-hexylcarbazole (3,6-DIHCz),<sup>50</sup> 2,3-bis(*N*-hexylcarbazol-3-yl)-*N*-cyclohexylmaleimide<sup>51</sup> and 2,7-dibromo-*N*-hexylcarbazole (2,7-DBrHCz)<sup>52</sup> were prepared following procedures from the literature. Each co-oligomer was prepared by two methods following previously reported procedures.<sup>53,54</sup>

**Synthesis of DICHMI.** A solution of 2,3-dibromo-*N*-cyclohexylmaleimide (5.06 g, 15.0 mmol) and sodium iodide (6.75 g, 45.0 mmol) in acetic acid (55 ml) was refluxed for 2 h. After the reaction mixture was then cooled to ambient temperature, the solvent was removed to give the crude product. The residue was recrystallized in ethyl acetate/*n*-hexane (1/10 = v/v) to yield yellow crystals (5.53 g, 12.8 mmol).

Yield 86%, m.p. 156–157 °C,  $R_f$  = 0.17 (silica gel TLC, *n*-hexane/dichloromethane = 1/2 (v/v)). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (p.p.m. from TMS): 1.10–1.42 (3H, m, cyclohexyl), 1.60–1.74 (3H, m, cyclohexyl), 1.76–1.92 (2H, m, cyclohexyl), 1.94–2.14 (2H, m, cyclohexyl) and 3.90–4.10 (1H, m, >N-CH of cyclohexyl group).

### Synthesis of 3,6-DBrMCz

**MCz.** A 200 ml flask equipped with a magnetic stirring bar was charged with a 60% dispersion of sodium hydride in mineral oil (5.19 g, 36.0 mmol). The mineral oil was removed by washing with three 10-ml portions of *n*-hexanes, allowing the sodium hydride to settle and withdrawing the supernatant solvent with a syringe. A solution of carbazole (5.03 g, 30.1 mmol) in dry *N,N*-dimethylformamide (DMF) (15 ml) was added to the suspension of sodium hydride in the 200-ml flask at 0 °C, and the mixture was stirred. After evolution of hydrogen ceased, a solution of methyl iodide (2.5 ml,

40.1 mmol) in dry DMF (15 ml) was added dropwise via an addition funnel at room temperature. After stirring for 1.5 h, the reaction mixture was quenched by the addition of water (50 ml) and then extracted with ethyl acetate. The combined organic layer dried over  $\text{MgSO}_4$ , and the solvent evaporated. The crude product was purified by recrystallization from ethyl acetate/*n*-hexane (1/10 = v/v) to yield colorless crystals.

Yield 72%, m.p. 78–80 °C,  $R_f$  = 0.20 (silica gel TLC, *n*-hexane/dichloromethane = 10/1 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 3.86 (3H, s, >N-CH<sub>3</sub>), 7.18–7.34 (2H, m, aromatic protons), 7.35–7.60 (4H, m, aromatic protons) and 8.10 (2H, d, aromatic protons).

3,6-DBrMCz. MCz (0.537 g, 3.00 mmol), NBS (1.33 g, 749 mmol) and pyridine (30 ml) were placed in a 100-ml three-necked flask, and then the mixture was refluxed at 120 °C. After 15 h, the reaction mixture was distilled to remove pyridine. The residue was dissolved in dichloromethane (50 ml) and washed with 3N HCl. The organic layer was dried over  $\text{MgSO}_4$ , and the solvent evaporated. The crude product was purified on a silica column using hexane/ethyl acetate (1/10 = v/v). A brown needle crystal product was obtained after removal of solvent.

Yield 45%, m.p. 155–157 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 3.82 (3H, s, >N-CH<sub>3</sub>), 7.27 (2H, d, aromatic protons), 7.54–7.61 (2H, dd, aromatic protons) and 8.13 (2H, d, aromatic protons).

#### Synthesis of 3,6-DIHCz

*N*-Hexylcarbazole (HCz). HCz (1.33 g, 5.29 mmol) was obtained as a colorless crystal in 88% yield from sodium hydride (60% oil) (0.326 g, 7.80 mmol) and carbazole (1.01 g, 6.03 mmol) with *n*-hexyl bromide (1.21 ml, 7.32 mmol), according to the above procedure for MCz.

Yield 88%, m.p. 59–61 °C,  $R_f$  = 0.55 (silica gel TLC, *n*-hexane/ethyl acetate = 10/1 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 0.85 (3H, t, -CH<sub>3</sub>), 1.20–1.46 (6H, m, alkyl chain protons), 1.78–1.94 (2H, m, >N-CH<sub>2</sub>-CH<sub>2</sub>-), 4.30 (2H, t, >N-CH<sub>2</sub>-), 7.22 (2H, d, aromatic protons), 7.44 (4H, dd, aromatic protons) and 8.10 (2H, d, aromatic protons).

3,6-DIHCz. *N*-hexylcarbazole (0.474 g, 1.88 mmol), potassium iodide (0.665 g, 4.01 mmol) and acetic acid (50 ml) were placed in a 100-ml flask and stirred at room temperature. After a few minutes, potassium iodate was added. After 24 h, the reaction mixture was distilled to remove acetic acid. The residue was dissolved in ethyl acetate and washed with water. The organic layer was dried over  $\text{MgSO}_4$ , and the solvent evaporated. The crude product recrystallized in ethyl acetate/*n*-hexane (1/10 = v/v) to yield colorless crystals (0.494 g, 0.981 mmol).

Yield 52%, m.p. 127–129 °C,  $R_f$  = 0.48 (silica gel TLC, *n*-hexane/ethyl acetate = 10/1 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 0.85 (3H, t, -CH<sub>3</sub>), 1.20–1.40 (6H, m, alkyl chain protons), 1.73–1.91 (2H, m, >N-CH<sub>2</sub>-CH<sub>2</sub>-), 4.22 (2H, t, >N-CH<sub>2</sub>-), 7.17 (2H, d, aromatic protons), 7.71 (2H, dd, aromatic protons) and 8.33 (2H, d, aromatic protons).

#### Synthesis of model compound

3-Bromo-*N*-hexylcarbazole. In a flask covered with aluminum foil, a stirred solution of HCz (2.01 g, 8.00 mmol) in  $\text{CHCl}_3$  (40 ml) was cooled to 0 °C. NBS (1.42 g, 7.99 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. The organic solvent was evaporated, and the residue was purified by extraction with diethyl ether and water. The organic layer was dried over  $\text{MgSO}_4$ , and the solvent evaporated. The crude product was purified on a silica column using *n*-hexane/ethyl acetate (1/10 = v/v). From NMR, the peaks of crude materials were confirmed, but we decided to advance to the next reaction by column chromatography in case of boron oxidation due to the ease of separation.

Yield 92%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 0.85 (3H, t, -CH<sub>3</sub>), 1.20–1.44 (6H, m, alkyl chain protons), 1.77–1.91 (2H, m, >N-CH<sub>2</sub>-CH<sub>2</sub>-), 4.24 (2H, t, >N-CH<sub>2</sub>-), 7.19–7.28 (2H, m, aromatic protons), 7.35–7.55 (3H, m, aromatic protons), 8.03 (1H, d, aromatic proton) and 8.19 (1H, d, aromatic proton).

*N*-hexylcarbazol-3-ylboronic acid. A solution of 3-bromo-*N*-hexylcarbazole (2.44 g, 7.38 mmol) in dry THF (30 ml) was cooled to –78 °C. *n*-Butyllithium

in *n*-hexane solution (1.65 mol l in *n*-hexane solution) (7.0 ml, 11.1 mmol) was slowly added dropwise via a syringe over 10 min. After complete addition, the reaction mixture was stirred for another hour. Triisopropyl borate (2.6 ml, 11.3 mmol) was then added at once. The mixture was allowed to warm to room temperature overnight. The reaction was finally quenched with 1N HCl and the mixture was poured into a large amount of water. After extraction with  $\text{CH}_2\text{Cl}_2$ , the organic layer was washed with water and dried over  $\text{MgSO}_4$ , and the solvent evaporated. Further purification by column chromatography (silica gel, *n*-hexane/dichloromethane, 2/1, v/v) afforded the product as a white solid. (0.976 g, 3.27 mmol).

Yield 44%, m.p. 198–202 °C.

2,3-Bis(*N*-hexylcarbazol-3-yl) *N*-cyclohexylmaleimide (model compound). Under a nitrogen atmosphere, a mixture of DICMI (0.173 g, 0.40 mmol), *N*-hexylcarbazol-3-ylboronic acid (0.239 g, 0.80 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  catalyst (0.0188 g, 0.0163 mmol) was stirred in dry toluene (6 ml).  $\text{K}_2\text{CO}_3$  (0.224 g, 1.62 mmol) in water (0.8 ml) was then added via a syringe. The reaction mixture was heated to 80 °C for 72 h. After cooling, the product was extracted with dichloromethane, washed with water and dried over  $\text{MgSO}_4$ , and the solvent evaporated. The crude product was purified on a silica column using *n*-hexane/dichloromethane (1/2 = v/v). The solution was concentrated, dissolved in a very small amount of THF and precipitated into 125 ml of methanol. The product was collected as a black powder and dried *in vacuo*. The pure compound was obtained (0.200 g, 0.30 mmol).

Yield 74%, m.p. 118–120 °C,  $R_f$  = 0.20 (silica gel TLC, *n*-hexane/dichloromethane = 2/1 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 0.85 (6H, t, -CH<sub>3</sub>), 1.14–1.48 (15H, m, cyclohexyl and *N*-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-), 1.66–1.79 (9H, m, cyclohexyl and >N-CH<sub>2</sub>-CH<sub>2</sub>-), 2.15–2.35 (2H, m, cyclohexyl), 4.09–4.20 (1H, m, >CH-), 4.26 (4H, t, >N-CH<sub>2</sub>-), 7.16–7.32 (4H, d, aromatic protons), 7.35–7.50 (4H, m, aromatic protons), 7.57 (2H, dd, aromatic protons), 8.00 (2H, d, aromatic protons), 8.43 (2H, d, aromatic protons).  $^{13}\text{C}$  ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 171.9, 140.9, 140.7, 134.5, 127.6, 125.9, 123.0, 122.7, 120.6, 119.9, 119.4, 108.9, 108.7, 51.2, 43.2, 31.5, 30.1, 28.9, 26.9, 26.2, 25.3, 22.5 and 14.0. High-resolution mass spectra (ESI M + H)  $m/z$  found, 678.4060, calculated for  $\text{C}_{46}\text{H}_{52}\text{N}_3\text{O}_2$ : 678.4060.

#### Synthesis of 2,7-DBrHCz

4,4'-Dibromo-2,2'-dinitrobiphenyl. A mixture of 1,4-dibromo-2-nitrobenzene (5.00 g, 17.8 mmol) and copper powder (2.51 g, 39.4 mmol) was stirred in 22 ml of DMF for 2 h at 125 °C. After cooling to room temperature, chloroform was added. The mixture was filtered with Celite 545. The filtrate was washed with water and brine, the solution dried over  $\text{MgSO}_4$  and the solvent evaporated. The crude product was recrystallized in ethyl acetate/*n*-hexane (1/10 = v/v) to yield light brown crystals (2.92 g, 7.26 mmol).

Yield 82%, m.p. 148–150 °C,  $R_f$  = 0.36 (silica gel TLC, (ethyl acetate/*n*-hexane = 1/5 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 7.16 (d, 2H, aromatic protons), 7.82 (dd, 2H, aromatic protons) and 8.38 (d, 2H, aromatic protons).

4,4'-Dibromo-2,2'-diaminobiphenyl. While a mixture of 4,4'-dibromo-2,2'-dinitrobiphenyl (2.91 g, 7.24 mmol), concentrated HCl (21 ml) and 35 ml of ethanol was stirred, small portions of tin powder (3.55 g, 29.9 mmol) were added to the reaction mixture. The reaction mixture was then refluxed for 2.5 h. The mixture was poured into cold water, and 2M NaOH solution was added to a pH of 8. The solution was extracted several times with chloroform. The combined organic layer was washed with water and dried over  $\text{Na}_2\text{SO}_4$ , and the solvent evaporated. The residue was dissolved in ethyl acetate, followed by precipitation with *n*-hexane to yield a yellow solid. The solid was filtered and washed with *n*-hexane to obtain the product (1.90 g, 5.56 mmol).

Yield 71%, m.p. 108–110 °C,  $R_f$  = 0.077 (silica gel TLC, (ethyl acetate/*n*-hexane = 1/10 (v/v)).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (p.p.m. from TMS): 3.74 (br, 4H, -NH<sub>2</sub>), 6.93 (s, 6H, aromatic protons).

2,7-Dibromocarbazole. A mixture of 4,4'-dibromo-2,2'-diaminobiphenyl (0.952 g, 2.78 mmol) and 19.8 ml of concentrated  $\text{H}_3\text{PO}_4$  was refluxed at 190 °C for 26 h. The crude product was added to water and removed by filtration. The residue was diluted with dichloromethane; the organic layer was



washed with water, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was dissolved in ethyl acetate, followed by precipitation with *n*-hexane to yield a yellow solid. The solid was filtered and washed with *n*-hexane to obtain the product (0.544 g, 1.67 mmol).

Yield 60%, m.p. 214–215 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (p.p.m. from TMS): 7.37 (dd, 2H, aromatic protons), 7.59 (d, 2H, aromatic protons), 7.89 (d, 2H, aromatic protons) and 8.07 (br, 1H, >NH).

**2,7-DBrHCz.** 2,7-DBrHCz (0.891 g, 2.18 mmol) was obtained as colorless crystals in 88% yield from sodium hydride (60% oil) ((0.355 g, 5.92 mmol), 2,7-dibromocarbazole (0.752 g, 2.31 mmol) with *n*-hexyl bromide (0.460 g, 2.79 mmol) according to the above procedure for MCz.

Yield 94%, m.p. 62–63 °C, *R*<sub>f</sub> = 0.42 (silica gel TLC, (*n*-hexane)). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (p.p.m. from TMS): 0.93 (t, 3H, -CH<sub>3</sub>), 1.40 (m, 6H, alkyl chain protons), 1.90 (m, 2H, >N-CH<sub>2</sub>-CH<sub>2</sub>-), 4.25 (t, 2H, >N-CH<sub>2</sub>-), 7.40 (dd, 2H, aromatic protons), 7.59 (d, 2H, aromatic protons) and 7.95 (d, 2H, aromatic protons).

#### Synthesis of polymer

**Poly(CHMI).** DICHMI (0.363 g, 0.842 mmol), COD (0.0978 g, 0.904 mmol), 2,2'-bipyridyl (0.146 g, 0.935 mmol), Ni(COD)<sub>2</sub> (0.347 g, 1.26 mmol), dry DMF (3 ml) and dry toluene (3 ml) were placed in a 50-ml sealed tube. The mixture was stirred at 60 °C for 72 h under a nitrogen atmosphere. The resultant mixture was poured into diethyl ether (100 ml). The solid that separated was filtered. The residue was dissolved in dichloromethane and washed with 1 N HCl and water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent evaporated. The crude product was dissolved in a very small amount of THF and precipitated into 125 ml of methanol. The product was collected as a black powder and dried *in vacuo*.

**Poly(3,6-HCz).** 3,6-DIHCz (0.403 g, 0.801 mmol), COD (0.104 g, 0.961 mmol), 2,2'-bipyridyl (0.142 g, 0.909 mmol), Ni(COD)<sub>2</sub> (0.332 g, 1.21 mmol), dry DMF (3 ml) and dry toluene (3 ml) were placed in a 50-ml sealed tube. The mixture was stirred at 80 °C for 72 h under a nitrogen atmosphere. The resultant mixture was poured into dichloromethane (100 ml) and washed with 1 N HCl and water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent evaporated. The crude product was dissolved in a very small amount of THF and precipitated into 125 ml of methanol. The product was collected as a white powder and dried *in vacuo*.

**Poly(CHMI-co-3,6-HCz).** *Typical procedure:* DICHMI (0.174 g, 0.404 mmol), 3,6-DIHCz (0.202 g, 0.401 mmol), COD (0.0973 g, 0.899 mmol), 2,2'-bipyridyl (0.142 g, 0.909 mmol), Ni(COD)<sub>2</sub> (0.332 g, 1.21 mmol), dry DMF (3 ml) and dry toluene (3 ml) were placed in a 50-ml sealed tube. The mixture was stirred at 80 °C for 72 h under a nitrogen atmosphere. The resultant mixture was poured into diethyl ether (100 ml). The solid that separated was filtered. The residue was dissolved in dichloromethane and washed with 1 N HCl and water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent evaporated. The crude product was dissolved in a very small amount of THF and precipitated into 125 ml of methanol. The product was collected as a brown powder and dried *in vacuo*.

**Poly(CHMI-co-2,7-HCz)** by another method. COD (0.133 g, 1.23 mmol), 2,2'-bipyridyl (0.188 g, 1.20 mmol), Ni(COD)<sub>2</sub> (0.332 g, 1.21 mmol) and dry DMF (3 ml) were placed in a 50 ml sealed tube. The mixture was stirred at 80 °C for 0.5 h under a nitrogen atmosphere, and then a mixture of DICHMI (0.174 g, 0.404 mmol) and 2,7-DBrHCz (0.164 g, 0.401 mmol) in dry DMF (3 ml) was added. The reaction was maintained at 80 °C for 24 or 48 h. The resultant mixture was poured into CH<sub>2</sub>Cl<sub>2</sub> (100 ml) and washed with 1 N HCl and water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent evaporated. The crude product was dissolved in a very small amount of THF and precipitated into 125 ml of methanol. The product was collected as a brown powder and dried *in vacuo*.

## RESULTS AND DISCUSSION

### Synthesis and characterization

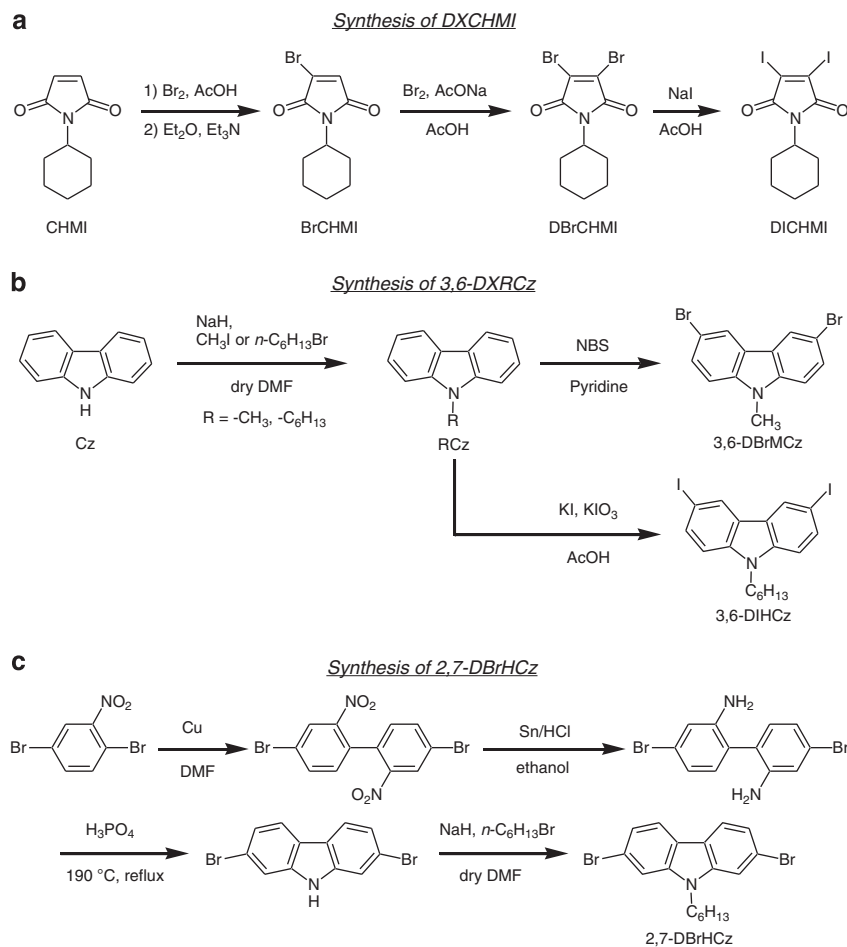
Scheme 2 illustrates the synthetic route for maleimide monomers and *N*-substituted carbazole derivatives. In the synthesis of DICHMI as

the key monomer, 2,3-dibromo-*N*-cyclohexylmaleimide was prepared by bromination of CHMI according to procedures from the literature.<sup>45</sup> The iodination of 2,3-dibromo-*N*-cyclohexylmaleimide with sodium iodide in acetic acid afforded DICHMI with high yield (86%). 3,6-DBrMCz and 3,6-DIHCz were synthesized by halogenation of the corresponding *N*-substituted carbazole derivatives. The alkylation of carbazole with methyl iodide and *n*-hexyl bromide in the presence of sodium hydride in DMF yielded MCz and *N*-hexylcarbazole, respectively. MCz was brominated by NBS in pyridine to obtain 3,6-DBrMCz. Diiodination of *N*-hexylcarbazole was performed in the presence of potassium iodide and potassium iodate in acetic acid, followed by recrystallization of the crude product to afford 3,6-DIHCz. However, 2,7-DBrHCz, which was substituted with bromide at the 2,7-positions, was prepared according to the procedures in the literature<sup>52</sup> and then obtained by alkylation under the same conditions as HCz described above.

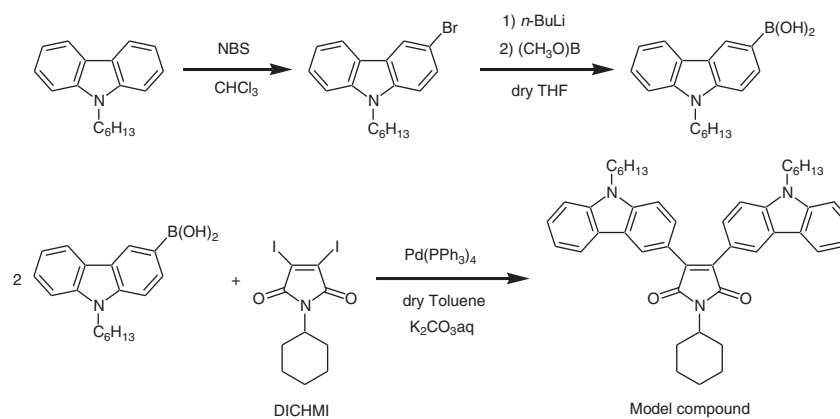
To reveal the relationship between the fluorescence and structure of conjugated co-oligomers, the authors prepared 2,3-bis(*N*-hexylcarbazol-3-yl)-*N*-cyclohexylmaleimide as a model conjugated co-oligomer containing CHMI and RCz units. The synthetic approach to the model compound is shown in Scheme 3. The model compound was synthesized in four steps from carbazole according to procedures from the literature.<sup>51</sup> Monobromination of *N*-hexylcarbazole was performed with NBS to yield 3-bromo-*N*-hexylcarbazole. The compound was used for the next step without any further purification. *N*-hexylcarbazole-3-ylboronic acid was synthesized via lithiation of 3-bromo-*N*-hexylcarbazole using *n*-butyllithium in *n*-hexane solution and subsequent boronation by triisopropyl borate in THF. Finally, a Suzuki-Miyaura coupling reaction of DICHMI with *N*-hexylcarbazole-3-ylboronic acid catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> in toluene produced the desired model compound.

All polymers were prepared by a Yamamoto coupling reaction catalyzed by bis(1,5-COD) nickel (0) with 1,5-COD and 2,2'-bipyridyl in a mixture of toluene and DMF. Furthermore, copolymerizations were performed under various feed ratios of [DICHMI]/[DXCz] = 0.33–3.00. All Yamamoto coupling polymerizations proceeded homogeneously throughout. After polymerization was complete, the polymerization mixtures were poured into a large amount of dichloromethane and washed with 1 N HCl and water. The organic phase was concentrated under vacuum. The resulting residue was dissolved in a small amount of THF and precipitated into excess MeOH. The results of the copolymerizations of DICHMI with dihalide carbazole derivatives are summarized in Table 1. Poly(CHMI) and poly(*N*-cyclohexylmaleimide-co-*N*-substituted carbazole)s were brown or black powders that were quite soluble in common organic solvents such as THF, CHCl<sub>3</sub>, toluene and DMF. The molar ratios of the CHMI unit in the co-oligomers (MI<sub>cont.</sub>) were determined by <sup>1</sup>H NMR and are shown in Table 1. An <sup>1</sup>H NMR spectrum of poly(CHMI-co-3,6-DMCz) obtained by the monomer molar ratio DICHMI/3,6-DBrMCz = 0.40/0.40 (mmol mmol<sup>-1</sup>) is shown in Figure 1. Three peaks in the aromatic region at 7.3–7.5, 7.6–8.0 and 8.1–8.6 p.p.m. were attributed to three different protons on the carbazole ring. The signals at 3.4–4.3 p.p.m. were assigned to a proton at the 1-position of the cyclohexyl substituent and methyl protons of the 3,6-carbazolene unit. The peaks at 0.8–2.4 p.p.m. were due to methylene protons of the cyclohexyl ring. In the same manner, the content (mol%) of CHMI units in other poly(*N*-cyclohexylmaleimide-co-*N*-substituted carbazole)s were also determined (Supplementary Figures S1–S3).

The homopolymerization of DICHMI resulted in low yield (Run 1). In the copolymerizations of CHMI with 3,6-DBrMCz (Runs 2–5),



Scheme 2 Synthetic route of monomers.



Scheme 3 Synthesis of the model compound.

$M_{\text{Icont.}}$  of CHMI were larger than the feed ratios of DICHMI/3,6-DBrMCz. The resulting lower polymerizabilities of 3,6-DBrMCz relative to DICHMI can be explained on the basis of the poor solubility of 3,6-DBrMCz. Thus, the number-average molecular weights ( $M_n$ ) of the resulting co-oligomers decreased with increasing feed ratios of 3,6-DBrMCz. However, co-oligomers obtained with

DICHMI and 3,6-DIHCz showed increased  $M_n$  and  $M_{\text{Icont.}}$  of the 3,6-HCz unit because of the improved solubility of 3,6-DIHCz bearing *n*-hexyl groups (Runs 6–8). As a result of copolymerization with 3,6-DIHCz, copolymerization with 2,7-DBrHCz was performed with a monomer molar ratio 0.40/0.40 (mmol mmol<sup>-1</sup>) so that maleimide and carbazole units could be introduced equally in the main chain.

**Table 1** Yamamoto coupling copolymerization of DICHMI with DXRCz<sup>a</sup>

Run	DXRCz	DICHMI /DXRCz (mmol mmol <sup>-1</sup> )	Time (h)	Yield <sup>b</sup> (%)	MI <sub>cont.</sub> <sup>c</sup> (mol%)	M <sub>n</sub> <sup>d</sup> (× 10 <sup>-3</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
1		0.80/—	72	11	100	1.6	1.23
2	3,6-DBrMCz	0.60/0.20	72	38	74	0.9	1.53
3		0.40/0.40	72	40	69	0.7	1.36
4		0.20/0.60	72	14	34	0.6	1.24
5		—/0.80	72	12	0	0.5	1.07
6	3,6-DIHCz	0.60/0.20	72	22	84	2.3	1.35
7		0.40/0.40	72	34	48	2.5	1.45
8		0.20/0.60	72	83	11	7.3, 2.6, 0.9	1.12, 1.10, 1.03
9		—/0.80	72	34	0	6.3, 2.4, 0.9	1.12, 1.10, 1.04
10	2,7-DBrHCz	0.40/0.40	72	51	31	2.8	1.63
11 <sup>e</sup>		0.40/0.40	24	68	40	2.0	1.50
12 <sup>e</sup>		0.40/0.40	48	34	48	2.4	1.60
13		—/0.80	72	78	0	1.6, 0.8	1.12, 1.02

Abbreviations: DICHMI, 2,3-diiodo-*N*-cyclohexylmaleimide; DMF, *N,N*-dimethylformamide; DXRCz, dihalide carbazole derivatives; GPC, gel permeation chromatography; <sup>1</sup>H NMR, proton nuclear magnetic resonance spectroscopy; M<sub>n</sub>, number-average molecular weights; M<sub>w</sub>, molecular weight; MI<sub>cont.</sub>, molar ratios of the CHMI unit in the co-oligomers.

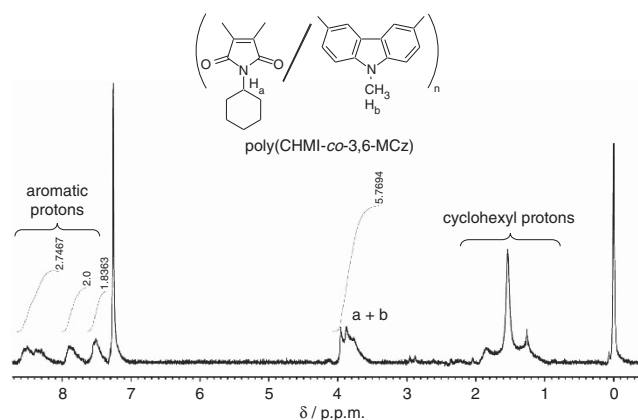
<sup>a</sup>Ni(COD)<sub>2</sub>, 1.20 mmol; conditions: temperature, 80 °C; solvents: toluene (3 ml) and DMF (3 ml).

<sup>b</sup>MeOH insoluble part.

<sup>c</sup>Determined by <sup>1</sup>H NMR.

<sup>d</sup>By GPC with poly(styrene) standard.

<sup>e</sup>Conditions: temperature, 80 °C; solvents: DMF.



**Figure 1** Proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) spectrum of poly(CHMI-co-3,6-MCz) (Table 1, Run 3) in CDCl<sub>3</sub>.

The yields of co-oligomers prepared from 2,7-DBrHCz and DICHMI under the same conditions were higher than that from 3,6-DIHCz (Runs 7 and 10). However, MI<sub>cont.</sub> of the co-oligomer with 2,7-DBrHCz was lower than that with 3,6-DIHCz. Torimitsu and co-workers<sup>54</sup> previously reported high molecular weights for poly(*N*-alkyl-3,6-carbazole)s. From this report, we performed the copolymerization of DICHMI with 2,7-DBrHCz by Torimitsu's method to improve the introduction of MI<sub>cont.</sub> MI<sub>cont.</sub> of the obtained copolymers increased relative to the MI<sub>cont.</sub> of copolymers obtained by previous methods. Formation of a dinickel-substituted complex with monomers that interfere with propagation of the polymer chain could be avoided by slowly adding the monomer solution into a hot nickel reagent solution.

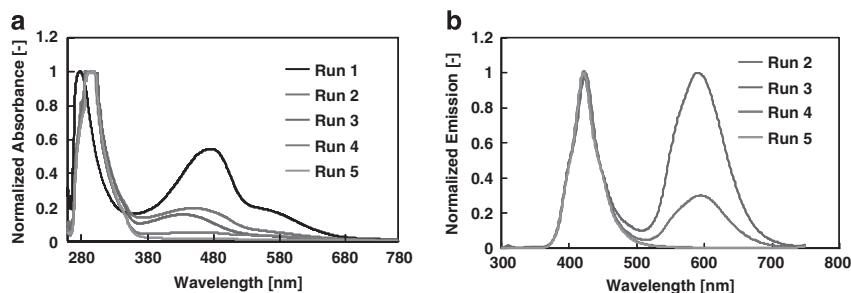
### Optical properties of co-oligomers

The normalized absorption (UV-vis) and PL spectra of co-oligomers and the model compound were measured in THF solution (concentration based on monomeric unit: 2.5 × 10<sup>-5</sup> M) and are illustrated in Figures 2–4. The photophysical properties of co-oligomers in dilute solutions are summarized in Table 2.

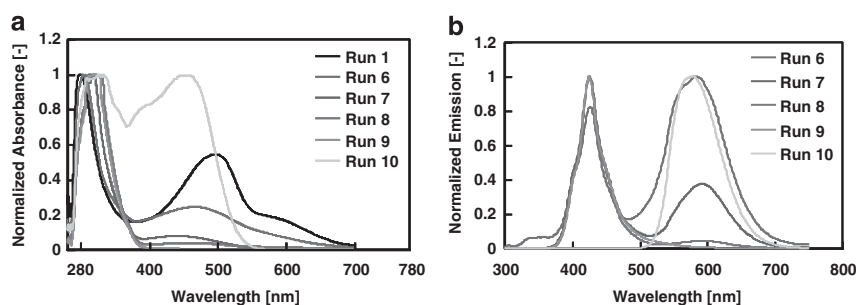
The UV-vis and PL spectra of co-oligomers obtained with 3,6-DBrMCz are shown in Figure 2. These co-oligomers exhibited absorption peaks attributed to the n-π\* transition of the carbonyl group and the π-π\* transition of the aromatic ring at approximately 306–310 nm and the conjugation of the main chain at approximately 454–474 nm (Figure 2a, Runs 2–4). In the PL spectra, poly(CHMI) showed no emission. However, co-oligomers showed two fluorescence peaks at approximately 422–424 and 590–595 nm (Figure 2b). Fluorescence peaks at long wavelengths were only observed for co-oligomers containing a large number of CHMI units (Runs 2 and 3).

The UV-vis and PL spectra of co-oligomers prepared from 3,6-DIHCz are shown in Figure 3 and Runs 6–8 in Table 2, similar to Runs 2–4. An absorption peak at long wavelength (Runs 7–9) exhibited a small blue-shift of approximately 6–24 nm in comparison with the peak from Run 6 because the main chains of the polymer were twisted by steric repulsion of bulky *n*-hexyl groups with increasing HCz unit content. Thus, the coplanarity of the main chain collapsed by a twist of the steric barrier, and the conjugated chain length was diminished. The UV-vis spectrum of the model compound showed two absorption peaks similar to those of the co-oligomers. However, the absorption peak at long wavelength showed broadening and increasing intensity (Figure 3, Run 10). The behaviors were explained by the lack of a steric barrier in the model compound, the coplanar structure, compared with the co-oligomers.

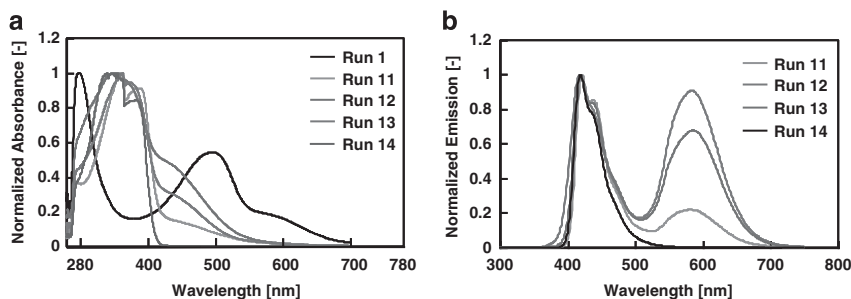
In the PL spectra, co-oligomers obtained from 3,6-DIHCz showed two fluorescence peaks at approximately 425–426 and 583–590 nm (Table 2, Runs 6–8). The intensities of co-oligomers (Runs 6 and 7)



**Figure 2** Normalized absorption (a) and emission (b) spectra of poly(CHMI) (Run 1) and poly(CHMI-co-3,6-MCz) (Runs 2–5 in Table 1) in tetrahydrofuran (THF) (concentration,  $2.5 \times 10^{-5} \text{ mol l}^{-1}$  based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.



**Figure 3** Normalized absorption (a) and emission (b) spectra of poly(CHMI) (Run 1), poly(CHMI-co-3,6-HCz) and model compound (Runs 6–10 in Table 1) in tetrahydrofuran (THF) (concentration,  $2.5 \times 10^{-5} \text{ mol l}^{-1}$  based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.



**Figure 4** Normalized absorption (a) and emission (b) spectra of poly(CHMI) (Run 1) and poly(CHMI-co-2,7-HCz) (Runs 11–14 in Table 1) in tetrahydrofuran (THF) (concentration,  $2.5 \times 10^{-5} \text{ mol l}^{-1}$  based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.

containing a large number of CHMI units ( $MI_{\text{cont.}} = 48\text{--}84$ ) in the long wavelength region increased (Figure 3b). The intensities of the peak at 583–590 nm affected the emission color. The homopolymer obtained from 3,6-DIHCz showed one fluorescence peak at approximately 425–426 nm (Figure 3, Run 9). However, the PL spectrum of the model compound featured a broad emission with maximum at 579 nm and emission color with very strong brightness unlike that of the co-oligomers (Figure 3, Run 9 and Figure 5). From these results, the fluorescence peak at approximately 425–426 nm was attributed to the emission of the conjugated structure of the neighboring HCz–HCz unit in co-oligomers, whereas the peak at approximately 583–590 nm was attributed to that of the CHMI–HCz unit.

Next, the UV–vis and PL spectra of the homo- and co-oligomers containing a 2,7-HCz unit are shown in Figure 4. The homopolymer

(poly(2,7-HCz)) exhibited an absorbance peak attributed to the  $\pi\text{--}\pi^*$  transitions of the  $\pi$ -conjugated main chain around 341 nm (Figure 4a, Run 14). The UV–vis spectra of co-oligomers showed shouldered peaks approximately 295 nm due to the  $n\text{--}\pi^*$  transitions of carbonyl groups and the  $\pi\text{--}\pi^*$  transitions of aromatic rings, and the absorption maxima were similar to poly(2,7-HCz) approximately 355–359 nm (Figure 4a, Runs 11–13). The UV–vis spectrum of poly(2,7-HCz), with maximum intensity at 341 nm, was blue-shifted by approximately 14–8 nm relative to that (355–359 nm) of poly(CHMI-co-2,7-HCz). The shouldered peaks of poly(CHMI-co-2,7-HCz) approximately 386–414 nm were attributed to the  $\pi\text{--}\pi^*$  transitions of the  $\pi$ -conjugated main chain by the neighboring CHMI–HCz unit, as there were no shouldered peaks for poly(2,7-HCz). The intensities of shouldered peaks approximately 386–414 nm increased with

**Table 2** UV-vis absorption and PL emission<sup>a</sup> maxima of poly(CHMI-co-Ar) and the model compound

Run	DXRCz	DICHMI /DXRCz (mmol mmol <sup>-1</sup> )	MI <sub>cont.</sub> <sup>b</sup> (mol%)	A <sub>max</sub> <sup>c</sup> (nm)	EW <sup>d</sup> (nm)	λ <sub>max</sub> <sup>e</sup> (nm)
1	—	0.8/—	100	299, 496	299	ND <sup>f</sup>
2	3,6- DBrMCz	0.6/0.2	74	315, 471	315	424, 595
3		0.4/0.4	69	316, 455	316	423, 590
4		0.2/0.6	34	316, 474	316	422
5	—	—/0.8	0	318	318	422
6	3,6-DIHCz	0.6/0.2	84	307, 465	307	426, 583
7		0.4/0.4	48	312, 441	312	425, 591
8		0.2/0.6	11	318, 459	318	426, 591
9	—	—/0.8	0	319	319	425
10	Model compound	—	—	312, 441	312	579
11	2,7-DBrHCz	0.4/0.4	31	359, 386	359	417, 581
12		0.4/0.4	40	355, 390	355	418, 583
13		0.4/0.4	48	355, 414	355	419, 585
14	—	—/0.8	0	341	341	419

Abbreviations: A<sub>max</sub>, absorption maximum peak; DICHMI, 2,3-diiodo-*N*-cyclohexylmaleimide; DXRCz, dihalide carbazole derivatives; EW, excitation wavelength; <sup>1</sup>H NMR, proton nuclear magnetic resonance spectroscopy; λ<sub>max</sub>, emission maximum peak; MI<sub>cont.</sub>, molar ratios of the CHMI unit in the co-oligomers; ND, not determined; PL, photoluminescence; THF, tetrahydrofuran; UV-vis, ultraviolet-visible.

<sup>a</sup>In all, 2.5 × 10<sup>-5</sup> mol l<sup>-1</sup> based on monomeric units in THF.

<sup>b</sup>Determined by <sup>1</sup>H NMR.

<sup>c</sup>A<sub>max</sub> = Absorption maximum peak.

<sup>d</sup>λ<sub>max</sub> = Emission maximum peak.

<sup>e</sup>E.W. = Excitation wavelength.

<sup>f</sup>nd: not determined.

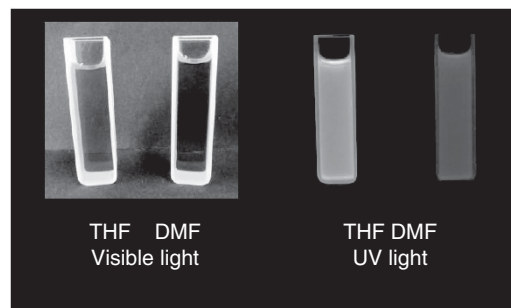
increasing MI<sub>cont.</sub>. In the PL spectra, co-oligomers exhibited two fluorescence peaks approximately 417–419 and 581–585 nm (Figure 4b, Runs 11–13). However, the PL spectrum of poly(2,7-HCz) exhibited one emission. Poly(2,7-HCz) and poly(CHMI-co-2,7-HCz) showed slightly blue-shifted maximum emission spectra (417–419 nm) in comparison with that of poly(CHMI-co-3,6-HCz) (424–427 nm). This result was attributable to the distinctive cross-linking position at a carbazole unit in the conjugated main chain. The photograph of poly(CHMI-co-RCz) (Table 2) in THF solution under the UV light (354 nm) is shown in Supplementary Figure S4.

### Fluorescence solvatochromism of co-oligomers

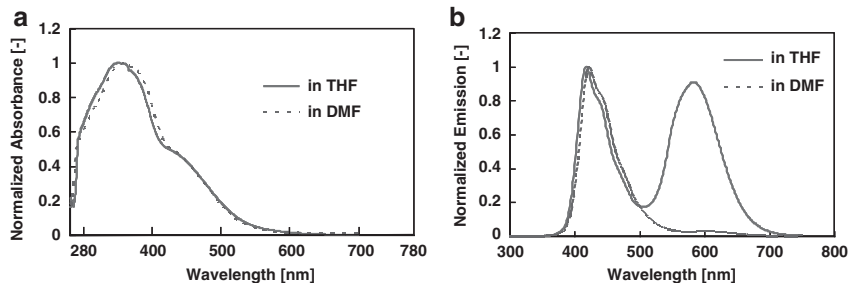
Interestingly, the emission properties of poly(CHMI-co-2,7-HCz) were significantly influenced by the nature of the solvent used, such as THF and DMF. The UV-vis and PL spectra of poly(CHMI-co-2,7-HCz) (Run 12) in THF and DMF are shown in Figure 5.

UV-vis spectra of poly(CHMI-co-2,7-HCz) measured in THF or DMF exhibited similar patterns. The PL spectrum in DMF exhibited a broad emission with a maximum at 422 nm, whereas that in THF was observed as two emission bands at 418 and 583 nm. The spectrum in DMF was similar to that of poly(2,7-HCz).

A photograph of poly(CHMI-co-2,7-HCz) in THF or DMF solution under visible and UV light (354 nm) is shown in Figure 6. The solutions of poly(CHMI-co-2,7-HCz) in THF and DMF were



**Figure 6** Photograph of poly(CHMI-co-2,7-HCz) (Run 12 in Table 2) under visible (right) and UV light (left) in tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF) (concentration, 2.5 × 10<sup>-5</sup> mol l<sup>-1</sup> based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.

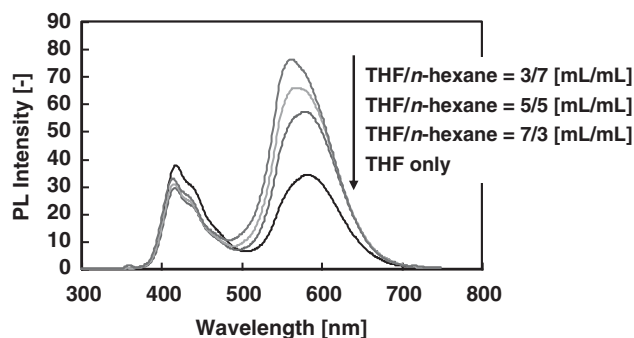


**Figure 5** Normalized absorption (a) and emission (b) spectra of poly(CHMI-co-2,7-HCz) (Run 12 in Table 2) in tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF) (concentration, 2.5 × 10<sup>-5</sup> mol l<sup>-1</sup> based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.

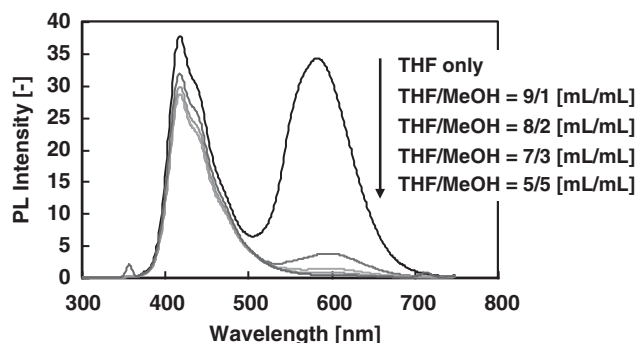


both yellow. Under UV irradiation, solutions of poly(CHMI-*co*-2,7-HCz) showed magenta emission in THF and blue emission in DMF, similar to the homopolymer. The fluorescence solvatochromism phenomenon occurred by decreasing emission bands at 583 nm only in highly polar solvents such as DMF.

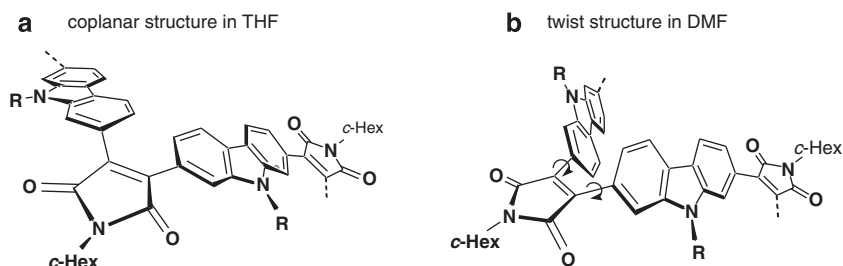
A change in the PL spectra by addition of *n*-hexane as a nonpolar solvent or MeOH as a polar solvent to THF solution was measured to investigate this phenomenon. PL spectra of Run 12 in THF/*n*-hexane are shown in Figure 7. An increase in the peak intensity at 583 nm was observed by increasing the *n*-hexane ratio. In addition, a change in the PL spectra by addition of MeOH as a



**Figure 7** Emission spectra of poly(CHMI-*co*-2,7-HCz) (Run 12 in Table 2) in a mixture of tetrahydrofuran (THF) and *n*-hexane (concentration,  $2.5 \times 10^{-5} \text{ mol l}^{-1}$  based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.



**Figure 8** Emission spectra of poly(CHMI-*co*-2,7-HCz) (Run 12 in Table 2) in a mixture of tetrahydrofuran (THF) and MeOH (concentration,  $2.5 \times 10^{-5} \text{ mol l}^{-1}$  based on monomeric units). A full color version of this figure is available at *Polymer Journal* online.



**Figure 9** Conformation change of CHMI-HCz bond by polarity of solvent (a) in tetrahydrofuran (THF) and (b) in *N,N*-dimethylformamide (DMF).

polar solvent to THF solution was investigated to explain this phenomenon. The PL spectra of Run 12 in THF/MeOH are shown in Figure 8. The peak intensity at 583 nm significantly decreased in THF/MeOH = 9/1 ( $\text{ml ml}^{-1}$ ) and was completely quenched in THF/MeOH = 5/5 ( $\text{ml ml}^{-1}$ ).

From the above results, the fluorescence peak intensity attributed to CHMI-HCz in poly(CHMI-*co*-2,7-HCz) clearly depended on the solvent polarity. The phenomenon presumably occurred by twisted intramolecular charge transfer states of CHMI-HCz units in the excited state. Twisted intramolecular charge transfer has been mainly observed in molecules with electron donor and acceptor units and was first acknowledged by the anomalous dual fluorescence of *p*-dimethylaminobenzonitrile in polar solvents.<sup>55</sup> Molecules forming twisted intramolecular charge transfer show new emission bands or quenching by twisting between donor and acceptor in polar solvents. In the spectra for poly(CHMI-*co*-2,7-HCz) obtained by this work, the fluorescence peak at 583 nm is quenched by the twist of CHMI-HCz (Figure 9).

## CONCLUSION

We prepared 3,6-DIHCz and 2,7-DBrHCz as dihalides with carbazolyl groups and performed Yamamoto coupling polymerizations with DICHMI. In the copolymerizations with 3,6-DBrMCz,  $M_n$  of the co-oligomers decreased with increasing feed ratios of 3,6-DBrMCz because of the low solubility of 3,6-DBrMCz. Yamamoto coupling polymerizations of CHMI with 3,6-DIHCz, which has better solubility, yielded co-oligomers with higher  $M_n$  and  $M_{I_{\text{cont}}}$  of the 3,6-HCz unit. The PL spectra of the resulting co-oligomers were measured in THF (concentration:  $2.5 \times 10^{-5} \text{ M}$ ) and showed intense fluorescence arranging from yellow to blue. The PL spectra of co-oligomers containing HCz units showed two fluorescence peaks approximately 425–426 and 583–590 nm. The intensities of fluorescence emissions were significantly affected by the polarity of organic solvents such as THF and DMF. It seems that the solvatochromic fluorescence phenomenon occurred by CHMI-HCz units in the excited state forming a twisted intramolecular charge transfer state in polar solvents such as DMF and MeOH. In this work, we have successfully and easily synthesized co-oligomers containing a maleimide moiety by Yamamoto coupling polymerizations with a dihalide aromatic compound. *N*-substituted maleimide acts as the electron acceptor, and control of the fluorescence wavelength of polymers is achieved by varying the feed ratio of [DICHMI]/[DXCz] and the solvent.

## ACKNOWLEDGEMENTS

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