Synthesis and Fluorescent Properties of Conjugated Copolymers Containing Maleimide and Fluorene Units at the Main Chain

Munetoshi Nakamura, Kazuhiro Yamabuki, Tsutomu Oishi, Kenjiro Onimura

Department of Applied Chemistry, Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi, 755-8611, Japan
Correspondence to: K. Onimura (E-mail: onimura@yamaguchi-u.ac.jp)

ABSTRACT: Yamamoto or Suzuki–Miyaura coupling polymerizations of 2,3-diiodo-N-cyclohexylmaleimide with fluorene derivatives (2,7-dibromo-9,9′-dihexylfluorene and 9,9′-dihexylfluorene-2,7-diboronic acid) were carried out. The number-average molecular weights (M_n) of the resulting copolymers were 2600–3500 by gel permeation chromatography analysis. The fluorescence emission of the alternating copolymer showed the emission maxima at 551 nm in THF. On the other hand, the random copolymers showed the bimodal emission peaks at 418–420 and 555–557 nm region, respectively. The fluorescence peaks of the random copolymers on the long wavelength region (555–557 nm) were attributed to the conjugated neighboring N-cyclohexylmaleimide-9,9′-dihexylfluorene units in the polymer main chain. Furthermore, the copolymers exhibited the fluorescence solvatochromism by the difference of the polarity of solvents. The alternating and random copolymers showed the different fluorescence solvatochromism, and the emission colors are distinguishable by the naked eye, respectively. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4945–4956

KEYWORDS: conjugated polymers; dyes/pigments; fluorene; fluorescence property; luminescence; N-substituted maleimide; solvatochromism; Suzuki–Miyaura coupling polymerization; Yamamoto coupling polymerization

INTRODUCTION Organic π-conjugated materials, especially polymers, are able to control not only the low cost and compatibility but also intrinsic property such as electronic, optical, conductivity, and stability by the structure design of the starting material. Thus, they find a variety of advanced technological applications in the fields of light-emitting diodes (PLEDs),[1–10] photovoltaics,[11–15] transistors,[16–18] and molecular electronics.[19–21] Among many promising conjugated polymers, polyfluorene, and its derivatives have been widely studied as emitting materials of organic electronics such as PLEDs because they show blue emission around at 420 nm, high PL, EL properties, and good thermal stability.[22–29] Recently, various polyfluorene derivatives containing the n-type semiconductor units such as benzothiadiazole, pyridine, naphthoselenadiazole, quinoxaline, and oxadiazole are reported.[30–34] On the basis of the idea of energy transfer from a electron donor to an acceptor molecule, copolymers consist of fluorene and n-type units show green, yellow, and even red emission compared with the blue emission polyfluorene.[32,35] In this way, the emission property of fluorene copolymer changes from blue to red color by the introduction of n-type unit.

Furthermore, fluorene copolymers are designed by the alternating or random polymerization. The random copolymer can induce various feed ratios of an acceptor unit over a wide range in comparison with the alternating one. Therefore, the design of the random copolymer is able to change the band gap of fluorene copolymer.[35,36] Also, the result that the introduction of an acceptor unit can lead to improve the electronic transport property of the random copolymer, and the copolymer is suitable for applications in multilayer PLEDs, is also reported.[33]

On the other hand, maleimide and its homopolymer are considered to be *cis*-olefin and consist of a repetition unit of the *cis* configuration like polyacetylene known as materials of the organic electronic device. Maleimide resembles n-type organic semiconductor materials such as phthalimide, naphthylimide, and pyreneimide for an electron-deficient heterocyclic ring.[37–41] For example, Cola and coworkers reported fluorescence sensors of the zinc ion by the maleimide derivative.[42] Furthermore, Chen and coworkers reported alternating copolymers obtained from N-substituted 2,3-diphenylmaleimide and boronate derivative of fluorene or bithiophene. The provided copolymer showed EL

Additional Supporting Information may be found in the online version of this article.

emissions of orange–red in the thin film.[43] This was the first report that maleimide copolymers showed PL and EL spectra at long wavelength and that maleimide comonomers were an important roles as an accepter 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 copolymer that maleimide is connected directly.[43–46]

In this article, the authors report Yamamoto and Suzuki–Miyaura cross-coupling polymerization of 2,3-diiodo-*N*-cyclohexylmaleimide (DICHMI) as an acceptor comonomer with fluorene derivatives (2,7-dibromo-9,9-dihexylfluorene or 9,9-dihexylfluorene-2,7-diboronic acid) as a donor comonomer, and examine polymerization properties and fluorescence properties of the copolymers obtained.

EXPERIMENTAL

Measurements

^{1}H (500 MHz) and ^{13}C (125 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA500 (JEOL) spectrometer using tetramethylsilane (TMS) (^{1}H NMR, δ 0.00) or CDCl$_3$ (^{13}C NMR, δ 77.0) as internal reference peaks at room temperature at the Collaborative Center for Engineering Research Equipment, Faculty of Engineering in Yamaguchi University. Splitting patterns are designated as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), and *br* (broad). Number-average-molecular (M_n) and molecular weight distributions (M_w/M_n) of polymers were obtained with gel permeation chromatography (GPC) on a CROMATO-PAC C-R7Ae plus (LC-10AS, CTO-2A, SPD-10A) equipped with polystyrene gel columns (HSG-40G, HSG-20G, HSG-15G, and HSG-10G), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1}, calibrated by polystyrene standards at 50 °C. The ultraviolet–visible (UV–vis) spectra were recorded on a UV-1650PC (Shimadzu Corporation) spectrometer. The photoluminescence (PL) spectra were recorded on a FP-6300 (JASCO Corporation) spectrophotometer.

Materials

All chemicals were used without any further purification. Fluorene, triisopropyl borate, and 1,5-cyclooctadiene (COD) were purchased from TCI. Potassium iodide and sodium iodide were available from Ishizu Seiyaku Lto. *N*-Bromosuccinimide was purchased from Wako Pure Chemical Industries. Sodium thiosulfate 5-hydrate, potassium carbonate, propylenecarbonate, and 2,2′-bipyridyl (α,α'-) were available from Kishida Reagents Chemicals. Bromine, potassium hydroxide, *n*-hexyl bromide, tetrakis(triphenylphosphine) palladium (0), and anhydrous magnesium sulfate (MgSO$_4$) were purchased from Nakalai Tesque. Triethylamine, *n*-butyllithium (*n*-BuLi), and bis(1,5-cyclooctadiene) nickel (0) were available from Kanto Chemical. *N*-Cyclohexylmaleimide was refined and used a thing offered by NOF Corporation. *n*-Hexane, ethyl acetate, THF, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dichloromethane, and chloroform were dried according to the standard procedure and distilled under nitrogen. Analytical thin-layer chromatography was performed on Merck silica gel plate 60F$_{254}$. Column chromatography was performed with silica gel 60 (0.063–0.200 mm, Merck).

DICHMI,[47,48] 2,7-dibromo-9,9′-dihexylfluorene (DBrDHF),[49,50] 9,9′-dihexylfluorene-2,7-diboronic acid (DHFDBa),[51] 2,3-bis(9,9-dihexylfluorene-3-yl)-*N*-cyclohexylmaleimide,[52,53] and each copolymers[35,54] were prepared by following the literature method.

Synthesis of 2,3-Diiodo-*N*-cyclohexylmaleimide

A solution of DBrCHMI (5.06 g, 15.0 mmol) and sodium iodide (6.75 g, 45.0 mmol) in acetic acid (55 mL) was heated at reflux for 2 h.[48] After that, removal of the solvent gave the crude product, which was purified by recrystallization from ethyl acetate/*n*-hexane (1/10 = v/v) to obtain a yellow crystal (5.53 g, 12.8 mmol).

Yield 86%. m.p. 156–157 °C. R_f = 0.17 (*n*-hexane/dichloromethane = 1/2). ^{1}H NMR (CDCl$_3$) δ (ppm from TMS): 1.10–1.42 (3H, m, cyclohexyl), 1.60–1.74 (3H, m,
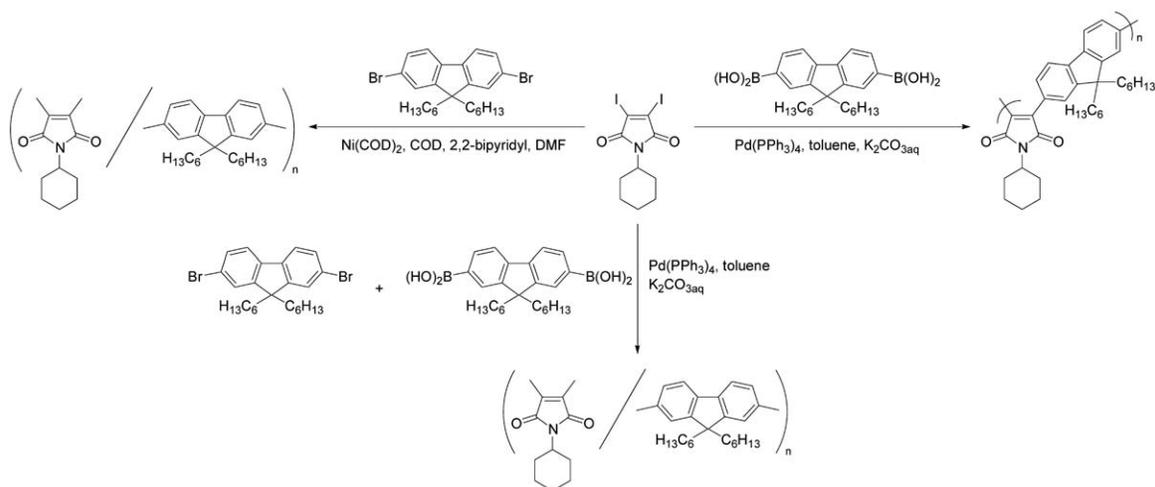

CHART 1 Yamamoto coupling polymerization of DICHMI with fluorene derivatives.

cyclohexyl), 1.76–1.92 (2H, m, cyclohexyl), 1.94–2.14 (2H, m, cyclohexyl), 3.90–4.10 (1H, m, =CH—).

Synthesis of 2,3-Bis(9,9-dihexylfluorene-3-yl)-*N*-cyclohexylmaleimide (Model Compound)

A mixture of DICHMI (0.173 g, 0.400 mmol), 9,9-dihexyl-fluorene-2-boronic acid[52] (0.303 g, 0.800 mmol), and Pd(PPh$_3$)$_4$ (0.0192 g, 0.0166 mmol) as catalyst was stirred in dry toluene (6 mL) under N$_2$. Then, K$_2$CO$_3$ (0.222 g, 1.61 mmol) was added in water (0.8 mL).[52,53] The reaction mixture was heated to 80 °C for 72 h. The reaction mixture was poured into dichloromethane (50 mL), and the combined organic layer was washed with water. The organic layer was dried over MgSO$_4$ and the solvent was evaporated. The crude product was purified on a silica gel column using *n*-hexane/dichloromethane (3/1 = v/v). The solution was concentrated, and dissolved in a small amount of THF, and precipitated into 125 mL of methanol. An orange powder was collected and dried *in vacuo*. An orange powder was obtained (0.209 g, 0.250 mmol).

Yield 62%. m.p. 118–120 °C. R_f = 0.12 (*n*-hexane/dichloromethane = 3/1). ^{1}H NMR (CDCl$_3$) δ (ppm from TMS): 0.46–0.68 (8H, m, hexyl), 0.76 (12H, t, hexyl), 0.91–1.17 (27H, m, cyclohexyl and hexyl), 1.22–1.45 (3H, m, cyclohexyl), 1.75–1.94 (12H, m cyclohexyl and hexyl), 2.16–2.29 (2H, m, cyclohexyl), 4.02–4.16 (1H, m, =CH—), 7.31 (6H, d, aromatic protons), 7.40–7.47 (4H, m, aromatic protons), 7.58 (2H, d, aromatic protons), 7.62–7.68 (2H, m, aromatic protons). ^{13}C (CDCl$_3$) δ (ppm from TMS): 171.0, 151.2, 150.7, 142,5, 140.3, 135.2, 129.0, 127.7, 126.9, 124.6, 122.9, 120.1, 119.6, 55.1, 51.2, 40.3, 31.6, 30.2, 29.7, 26.1, 25.2, 23.8, 22.6, 14.0.

Synthesis of Polymers

Poly(CHMI)

COD (0.132 g, 1.22 mmol), 2,2'-bipyridyl (0.188 g, 1.20 mmol), Ni(COD)$_2$ (0.331 g, 1.20 mmol), and dry DMF (3 mL) were placed in a 50-mL schlenk flask.[35,54] The mixture was stirred at 60 °C for 0.5 h under a nitrogen atmosphere, and then DICHMI (0.174 g, 0.803 mmol) in dry DMF (3 mL) was added. The reaction was maintained at 60 °C for 48 h. The resultant mixture was poured into the dichloromethane (50 mL), and washed with 1*N* HCl and water. The organic layer dried over MgSO$_4$ and the solvent evaporated. The crude product was dissolved in a small amount of THF, and precipitated into 125 mL of methanol. The product was collected as a black powder and dried *in vacuo*.

Poly(DHF)

COD (0.132 g, 1.22 mmol), 2,2'-bipyridyl (0.187 g, 1.20 mmol), Ni(COD)$_2$ (0.331 g, 1.20 mmol), and dry DMF (3 mL) were placed in 50-mL schlenk flask. The mixture was stirred at 60 °C for 0.5 h under a nitrogen atmosphere, and then DBrDHF (0.397 g, 0.806 mmol) in dry DMF (3 mL) was added. The reaction was maintained at 60 °C for 48 h. The resultant mixture was poured into the dichloromethane (50 mL), and washed with 1*N* HCl and water. The organic layer dried over MgSO$_4$ and the solvent evaporated. The crude

product was dissolved in a 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-DHF) by Yamamoto Coupling Reaction

COD (0.132 g, 1.22 mmol), 2,2'-bipyridyl (0.189 g, 1.21 mmol), Ni(COD)$_2$ (0.332 g, 1.21 mmol), and dry DMF (3 mL) were placed in a 50-mL schlenk flask. The mixture was stirred at 60 °C for 0.5 h under a nitrogen atmosphere, and then a mixture of DICHMI (0.174 g, 0.405 mmol), 2,7-DBrDHF (0.197 g, 0.401 mmol) in dry DMF (3 mL) was added. The reaction was maintained at 60 °C for 24–48 h. The resultant mixture was poured into the dichloromethane (50 mL), and washed with 1*N* HCl and water. The organic layer dried over MgSO$_4$ and the solvent evaporated. The crude product was dissolved in a 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-alt-DHF) by Suzuki–Miyaura Coupling Reaction

A mixture of DICHMI (0.173 g, 0.400 mmol), DHFDBa (0.170 g, 0.402 mmol), Pd(PPh$_3$)$_4$ catalyst (0.0185 g, 0.0160 mmol), and dry toluene (6 mL) was placed in a 50-mL schlenk flask. Then, K$_2$CO$_3$ (0.225 g, 1.63 mmol) in water (1.6 mL) was added via syringe. The mixture was stirred at 90 °C for 48 h under N$_2$. The reaction mixture was poured into dichloromethane (50 mL) and washed with water. The organic layer was dried over MgSO$_4$ and the solvent was evaporated. The crude product was dissolved in a 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-DHF) by Suzuki–Miyaura Coupling Reaction

A mixture of DICHMI (0.0874 g, 0.203 mmol), DBrDHF (0.0992 g, 0.201 mmol), DHFDBa (0.170 g, 0.402 mmol), and Pd(PPh$_3$)$_4$ (0.0187 g, 0.0162 mmol) dry toluene (6 mL) was placed in a 50-mL schlenk flask. Then, K$_2$CO$_3$ (0.221 g, 1.60 mmol) in water (1.6 mL) was added via syringe. The mixture was stirred at 90 °C for 48 h under N$_2$. The resultant mixture was poured into dichloromethane (50 mL), and washed with water. The organic layer was dried over MgSO$_4$ and the solvent was evaporated. The crude product was dissolved in a small amount of THF, and precipitated into 125 mL of methanol. The product was collected as a brown powder and dried *in vacuo*.

RESULT AND DISCUSSION

Synthesis and Characterization

Scheme 1 illustrates the synthetic route for maleimide monomers and fluorene derivatives. In the synthesis of DICHMI as the key monomer, 2,3-dibromo-*N*-cyclohexylmaleimide (DBrCHMI) was prepared by bromination of *N*-cyclohexylmaleimide (CHMI) according to the literature.[47] The iodination of DBrCHMI with sodium iodide in acetic acid afforded DICHMI in good yield (86%). 2,7-Dibromo-9,9-dihexylfluorene (DBrDHF) was synthesized from fluorene by bromination with bromine in CHCl$_3$ and alkylation with KOH in DMSO. 9,9-Dihexylfluorene-2,7-diboronic acid (DHFBa) was

a) Synthesis of DXCHMI
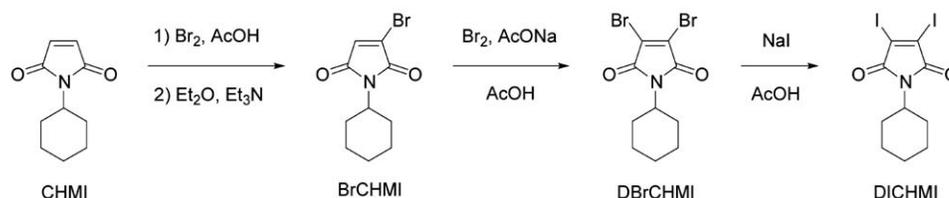
b) Synthesis of DBrDHF and DHFDBa
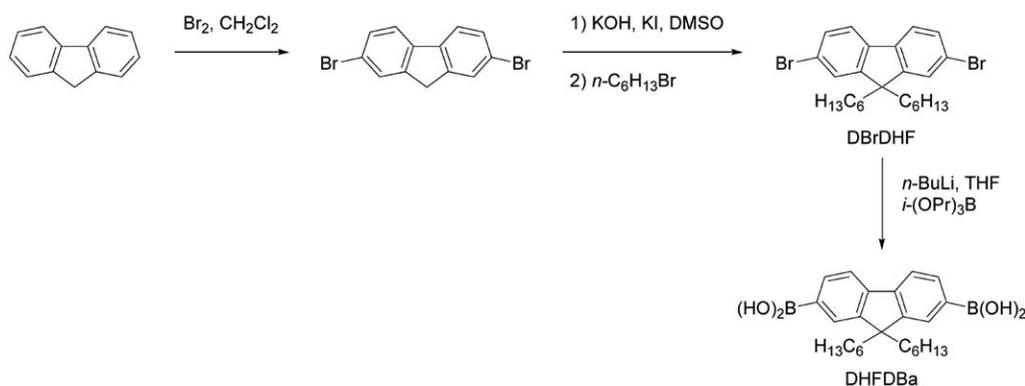
SCHEME 1 Synthetic route of monomers.

synthesized via lithiation of DBrDHF using *n*-BuLi, and then boronation by triiropropyl borate in THF.

In order to reveal relationship between properties of fluorescence and structures of resulting copolymers, the authors prepared 2,3-bis(9,9-dihexylfluorene-3-yl)-*N*-cyclohexylmaleimide as a model compound of conjugated copolymers containing a CHMI and a DHF unit. The synthetic approach to a model compound is presented in Scheme 2. The model compound was synthesized in four steps from fluorene according to the literature procedures.[52,53] A monobromination of fluorene was carried out by NBS in propylenecarbonate (PC) to give 2-bromofluorene. 2-Bromo-9,9-dihexylfluorene and 9,9-dihexylfluorene-2-boronic acid were synthesized from 2-bromofluorene described above. Finally, Suzuki–Miyaura coupling reaction of DICHMI and 9,9-dihexylfluorene-2-boronic acid catalyzed by Pd(PPh$_3$)$_4$ in toluene produced a desired model compound.

The copolymers were prepared from DICHMI, DBrDHF, and DHFDBa by Yamamoto or Suzuki–Miyaura coupling polymerization. In Yamamoto coupling reaction, the copolymerization was carried out in the presence of each comonomer of DICHMI and DBrDHF (monomer feed ratio was 0.40/0.40 [mmol/mmol]), bis(cyclooctadiene)nickel as a catalyst, and 2,2′-bipyridyl and 1,5-COD as a ligand in DMF. On the other hand, in Suzuki–Miyaura coupling, the copolymerization was

carried out in the presence of comonomers of DICHMI and DHFDBa (monomer feed ratio was 0.40/0.40 [mmol/mmol]), tetrakis(triphenylphosphine)palladium as a catalyst, and potassium carbonate as a base in a mixed solution of toluene and water. In addition, in Suzuki–Miyaura coupling, the copolymerization was also carried out using DICHMI, DBrDHF, and DHFDBa (DICHMI/DBrDHF/DHFDBa = 0.20/0.20/0.40 [mmol/mmol/mmol]). In these polymerizations, the random copolymers were obtained along with the resulting copolymer by Yamamoto coupling reaction. After the end of polymerization, metal catalysts were removed by washing the reaction mixture with 1*N* HCl. The organic phase was evaporated *in vacuo*. The residue was purified by reprecipitation method with excess MeOH. The results of the copolymerization of DICHMI with fluorene derivatives are summarized in Table 1. Copolymers were white or brown powders, which were quite soluble in common organic solvents such as THF, CHCl$_3$, and DMF. Interestingly, these copolymers showed solubility in *n*-hexane. This solubility in *n*-hexane was due to the presence of the long alkyl chains of fluorene units. The ratios of a CHMI unit in copolymers (MI$_{cont.}$) were determined by ^{1}H NMR and were shown in Table 1. ^{1}H NMR spectra of poly(CHMI-*co*-DHF) (Table 1, Run 4) and poly(CHMI-*alt*-DHF) were shown in Figure 1. A broad peak in the aromatic region at 7.3–8.0 ppm was attributed to protons on the fluorene ring. A signal at 3.9–4.2 ppm
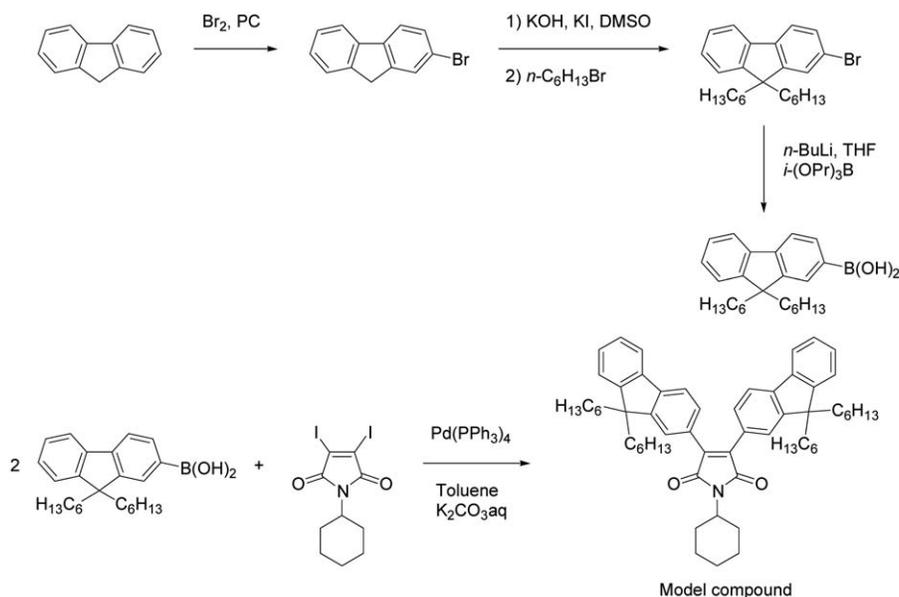
SCHEME 2 Synthesis of model compound.

was assigned to a proton at the 1-position of the cyclohexyl substituent. Peaks at 0.5–2.3 ppm were due to methylene protons of the cyclohexyl ring and *n*-hexyl on the side chain in a fluorene unit. In the same manner, the contents (mol %) of CHMI units in other poly(CHMI-*co*-DHF)s were also determined in Figure 1(a). ^{1}H NMR spectrum of poly(CHMI-*alt*-DHF) was shown in Figure 1(b). In addition, ^{13}C NMR spectra of copolymers (Table 1, Runs 3 and 5) were shown in Figures S1 and S2.

The homopolymer of DICHMI was obtained in low yield and number average molecular weight compared with poly(DHF) (Table 1, Runs 1, 2). In the copolymerization of DICHMI with DBrDHF, the number average molecular weights (M_ns) increased with increasing polymerization times (Table 1, Runs 3 and 4). But MI$_{cont.}$ and yield slightly decreased with increasing polymerization times. The copolymers by Suzuki–Miyaura coupling reaction were obtained in good yield (70–78%) and confirmed a small improvement of M_n in compari-

son with ones by Yamamoto coupling reaction (Table 1, Runs 5 and 6). The authors were reported that the low polymerizablites of 2,3-dihalido-*N*-substituted maleimide were responsible for side reactions such as a dehalogenation at the terminal end.[47(b)] The homopolymerizations and copolymerizations of DICHMI proceeded by side reactions such as a dehalogenation in this article.

Optical Properties of Copolymers

The normalized absorption (UV–vis) and PL spectra of copolymers and a model compound were measured in a THF solution (concentration based on monomeric unit: 2.5×10^{-5} mol L^{-1}), and illustrated in Figure 2. The photophysical properties of copolymers in a dilute solution are summarized in Table 2.

The homopolymer of DICHMI showed absorption peaks at 299 nm and 496 nm, which were attributed to the π–π^* transition of enone groups and the π–π^* transition of the conjugated main chain, respectively [Fig. 2(a), Run 2]. The

TABLE 1 Copolymerization of DICHMI with Fluorene Derivatives

Run		Time (h)	Yield[a] (%)	MI$_{cont.}$[b] (mol %)	M_n[c] $\times 10^{-3}$	M_w/M_n[c]
1	Poly(CHMI)[d]	48	13	100	1.0	1.1
2	Poly(DHF)[e]	48	87	0	17.0, 4.1	1.3, 1.1
3	Poly(CHMI-*co*-DHF)[f]	24	60	44	2.6	1.6
4	Poly(CHMI-*co*-DHF)[f]	48	52	40	3.0	1.4
5	Poly(CHMI-*alt*-DHF)[g]	48	78	50	3.5	1.4
6	Poly(CHMI-*co*-DHF)[h]	48	70	24	2.6	1.4

[a] MeOH insoluble part.
[b] By ^{1}H NMR.
[c] By GPC with poly(styrene) standard.
[d] Yamamoto coupling polymerization of DICHMI.
[e] Yamamoto coupling polymerization of DBrDHF.

[f] Yamamoto coupling polymerization of DICHMI and DBrDHF.
[g] Suzuki–Miyaura coupling polymerization of DICHMI and DHFDBa.
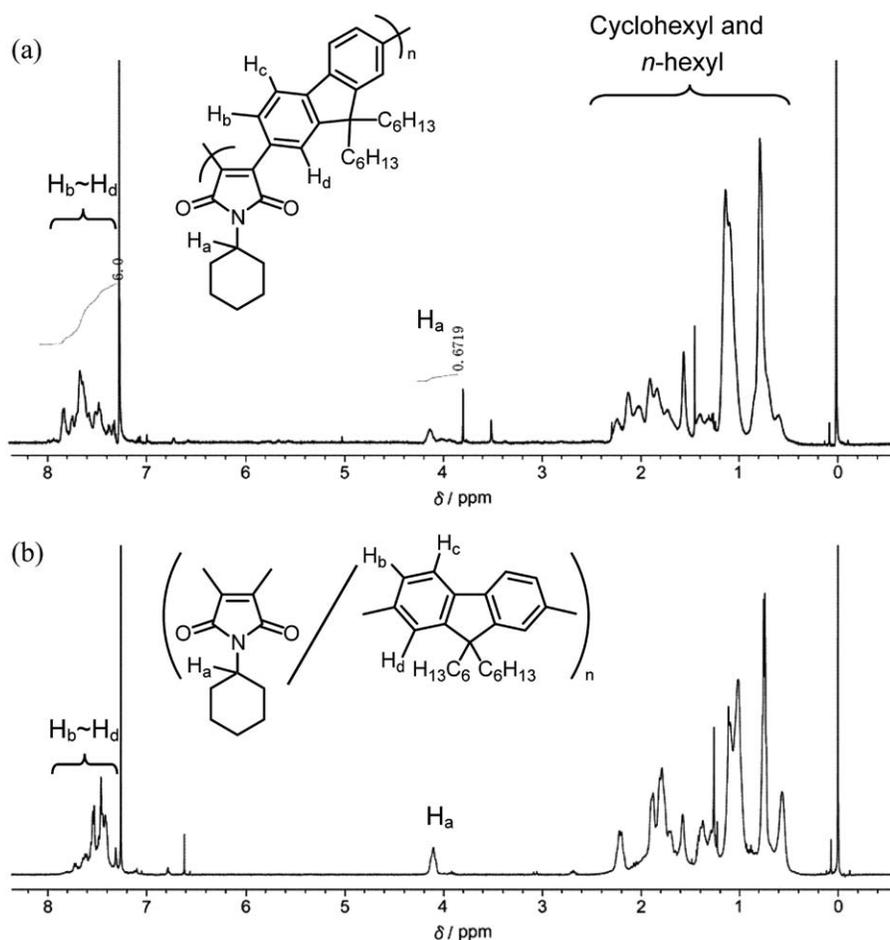[h] Suzuki–Miyaura coupling polymerization of DICHMI, DBrDHF, and DHFDBa.

FIGURE 1 ^{1}H NMR spectra of (a) poly(CHMI-*co*-DHF) (Table 1, Run 4) and (b) poly(CHMI-*alt*-DHF) (Table 1, Run 5) in CDCl$_3$.

homopolymer of DBrDHF showed absorption peaks at 339 and 397 nm attributed to the π–π^* transition of aromatic rings of fluorene and conjugated chain [Fig. 2(a), Run 3]. The model compound showed broad peaks at 317 and 411 nm [Fig. 2(a), Run 1]. The copolymers by Yamamoto coupling reaction exhibited shoulder peaks attributed to the n–π^*

transition of carbonyl groups and the π–π^* transition of aromatic rings of fluorene at around 303 nm [Fig. 2(a), Runs 4 and 5]. Further, the copolymers showed the maximum and shoulder peaks at around 364 and 440 nm, respectively. On the other hand, in the copolymers by Suzuki–Miyaura coupling reaction, the alternating copolymer showed a spectrum
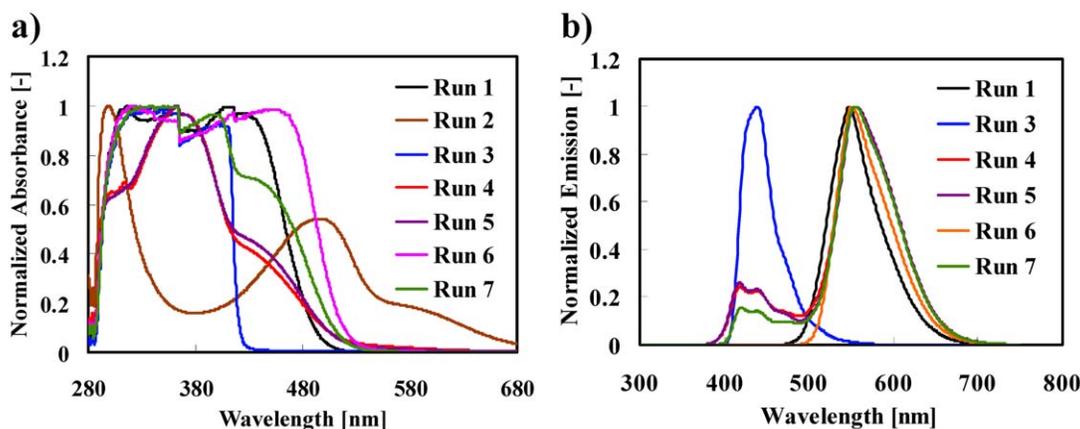

FIGURE 2 Normalized absorption (a) and emission (b) spectra of poly(CHMI) (Run 2), poly(DHF) (Run 3), and copolymers (Runs 4–7) and model compound (Run 1 in Table 2) in THF (concentration; 2.5 × 10^{-5} mol L^{-1} base on monomeric units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 UV–Vis Absorption and PL Emission Spectral Data for the Copolymers and Model Compound in THF[a]

Run		Time[b] (h)	MI$_{cont.}$[c] (mol %)	$\lambda_{abs.}$[d] (nm)	E.W.[e] (nm)	$\lambda_{Em.}$[f] (nm)
1	Model compound	–	–	317, 411	411	548
2	Poly(CHMI) [g]	48	100	299, 496	299	nd[h]
3	Poly(DHF)[i]	48	0	339, 397	397	419
4	Poly(CHMI-*co*-DHF)[j]	24	44	302, 365	365	418, 556
5	Poly(CHMI-*co*-DHF)[j]	48	40	304, 363	363	418, 557
6	Poly(CHMI-*alt*-DHF)[k]	48	50	321, 440	440	551
7	Poly(CHMI-*co*-DHF)[l]	48	24	338, 398, 433	398	420, 555

[a] 2.5×10^{-5} mol L^{-1} based on monomeric units in THF.
[b] Time = polymerization time.
[c] By determined by ^{1}H NMR.
[d] $\lambda_{abs.}$ = absorption peaks.
[e] E.W. = excitation wavelength.
[f] $\lambda_{Em.}$ = emission peaks.
[g] Yamamoto coupling polymerization of DICHMI.

[h] nd, not determined.
[i] Yamamoto coupling polymerization of DBrDHF.
[j] Yamamoto coupling polymerization of DICHMI and DBrDHF.
[k] Suzuki–Miyaura coupling polymerization of DICHMI and DHFDBa.
[l] Suzuki–Miyaura coupling polymerization of DICHMI, DBrDHF, and DHFDBa.

pattern similar to the model compound [Fig. 2(a), Runs 1 and 6]. But, the absorption peak on the part of the long wavelength showed a red shift about 30 nm in comparison with the model compound. This red shift was thought to be due to the extension of conjugated chains by the polymerization. The random copolymer by Suzuki–Miyaura coupling reaction showed absorption peaks at 338 and 398 nm, and a shoulder peak was observed at 433nm [Fig. 2(a), Run 7]. From the above UV–vis spectra, the alternating copolymer showed the recognizable absorption peak attributed to the conjugated main chain on the long wavelength region. Meanwhile, the random copolymers showed a shoulder peak on the long wavelength region. A coplanarity of the conjugated main chain was collapsed by a twist with the presence of a continuous DHF unit in the random copolymers. Thus, the effective conjugation length of random copolymers was shorter than alternating one, and the absorption peak on the long wavelength region was shoulder.

In PL spectra, the homopolymer of DICHMI showed no emission property. The homopolymer of DBrDHF showed an emission peak at 419 nm [Fig. 2(b), Run 3]. The model compound and the alternating copolymer exhibited emission peaks at around 548–551 nm [Fig. 2(b), Runs 1 and 7]. This red shift of about 120 nm in comparison with the homopoly-

mer of DBrDHF is considered to be attributed an intramolecular donor/acceptor influence in the presence of an *N*-cyclohexylmaleimide-9,9′-dihexylfluorene (CHMI-DHF) unit. On the other hand, the random copolymers by Yamamoto coupling reaction showed the bimodal emission peaks at the position each similar to the homopolymer of DBrDHF and the model compound. The change of emission spectra was not seen by difference of polymerization time [Fig. 2(b), Runs 5 and 6]. In addition, the random copolymer by Suzuki–Miyaura coupling reaction showed the modest reduction of the emission peak on the part of the short wavelength in comparison with one by Yamamoto coupling reaction. Judging from the above results, it was thought that emission peaks of the random copolymers on the short wavelength region were attributed to the fluorene unit and the others were attributed to CHMI-DHF unit in the main chain.

Fluorescence Solvatocromism of the Copolymers in Various Solvent
As described above, the resulting copolymers showed high solubility in *n*-hexane along with THF and DMF. Furthermore, emission colors of these copolymers were different in various organic solvent. The UV–vis and PL spectra of the alternating copolymer and the model compound in *n*-hexane,

TABLE 3 UV–Vis Absorption and PL Emission Spectral Data for Poly(CHMI-*alt*-DHF) and Model Compound in Various Solvent[a]

Run		Solv.	$\lambda_{abs.}$[b] (nm)	E.W.[c] (nm)	$\lambda_{Em.}$[d] (nm)
1	Model compound	*n*-Hexane	315, 416	416	540
2	Model compound	THF	317, 411	411	548
3	Model compound	DMF	313, 414	414	553
4	Poly(CHMI-*alt*-DHF)	*n*-Hexane	308, 434	434	545
5	Poly(CHMI-*alt*-DHF)	THF	321, 452	452	551
6	Poly(CHMI-*alt*-DHF)	DMF	308, 433	433	559

[a] 2.5×10^{-5} mol L^{-1} based on monomeric units in various solvent.
[b] $\lambda_{abs.}$ = absorption peaks.

[c] E.W. = excitation wavelength.
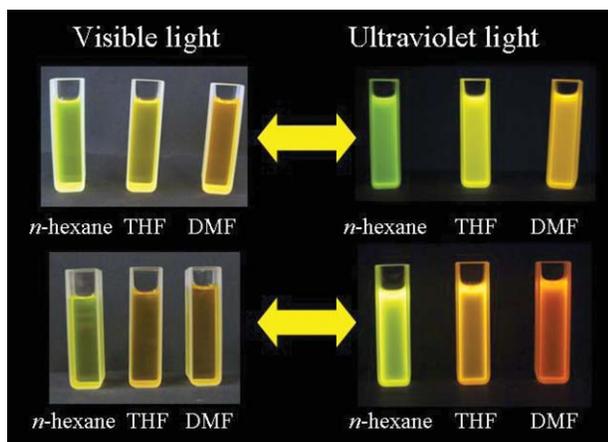[d] $\lambda_{Em.}$ = emission peaks.

FIGURE 3 Photographs of poly(CHMI-*alt*-DHF) (top) and model compound (bottom) under the visible light (left) and the UV light (right) in various solvent (concentration; 2.5×10^{-5} mol L^{-1} base on monomeric units).

THF, and DMF are measured, and the measurement results are summarized in Table 3.

In UV–vis spectra, the model compound exhibited similar spectra in various kinds of solvent (Table 3, Runs 1–3). On the other hand, the alternating copolymer showed the change of the absorption peak attributed to the conjugated main chain on the long wavelength region (Table 3, Runs 4–6). The peaks were observed to the red shift of about 20 nm and increasing of peak intensity in comparison with *n*-hexane and DMF when the measurement solvent was THF (Table 3, Run 5). In PL spectra, the emission peaks of the alternating copolymer and the model compound showed a red shift with increasing the polarity of solvents such as THF and DMF. The photographs of the solution of the alternating copolymer and model compound in various solvents under a visible light and a UV light are shown in Figure 3. The emission colors of the alternating copolymer and model compound observed by the naked eye showed the bathochromic shift. From the photographs and the

emission spectra, it seemed that emission properties of the alternating copolymer and model compound were dependent on the polarity of solvents.

The UV–vis and emission spectra of the random copolymer and model compound in *n*-hexane, THF, and DMF are showed in Figures 4 and 5, and the measurement results are summarized in Table 4. The photographs of the solution of the random copolymers in various solvents under a UV light are shown in Figure 6.

Spectral patterns of the absorbance peaks of the random copolymers by Yamamoto coupling reaction did not change by changing the measurement solvent [Fig. 4(a), Runs 4–9]. However, the PL spectra of random copolymers showed the significant change. The random copolymers showed bimodal emission peaks in THF, but the peaks on the long wavelength region remarkably increased in *n*-hexane and decreased in DMF [Fig. 4(b), Runs 4–9]. Along with a change of this spectral pattern, the emission colors observed by the naked eye were very different, and the copolymers showed yellow in *n*-hexane, orange in THF and blue in DMF, respectively (Fig. 6, left). In this bimodal emission peaks, one on the short wavelength region was attributed to fluorene units and the other on the long wavelength region was attributed to CHMI-DHF units in the main chain from the above. In emission peaks, kinds of solvent gave the strongest influence to the peak on the long wavelength region. Thus, the authors clarified that CHMI-DHF units in the main chain affected some sorts of solvent effect.

The random copolymers by Suzuki–Miyaura coupling reaction were affected by kinds of solvent on UV–vis spectra. The absorption peaks attributed to the conjugated main chain at around 422–433 nm decreased with increasing the polarity of solvent [Fig. 5(a), Runs 10–12]. Meanwhile, an emission peak on the long wavelength region increased in nonpolar solvent and decreased in polar solvent along with the random copolymers by Yamamoto coupling reaction [Fig. 5(b), Runs 10–12]. However, the peak intensity on the short
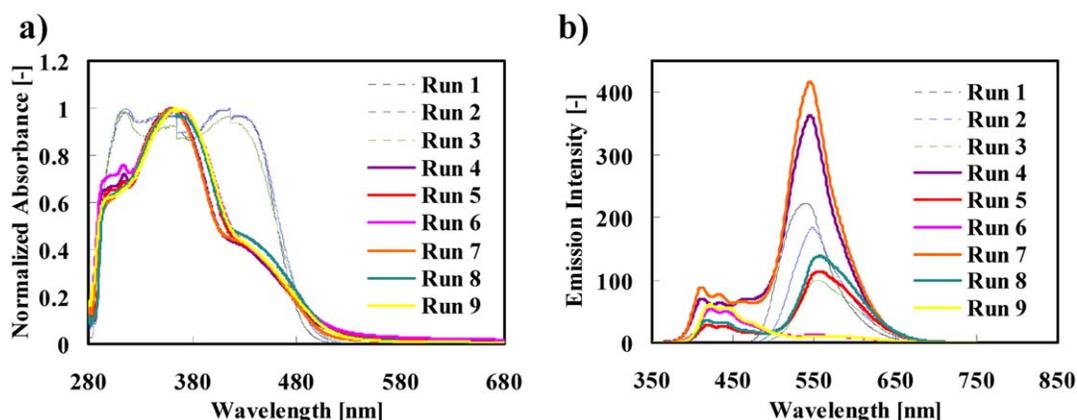

FIGURE 4 Normalized absorption (a) and emission (b) spectra of poly(CHMI-*co*-DHF) by Yamamoto coupling reaction (Runs 4–9) and model compound (Runs 1–3 in Table 4) in various solvent (concentration; 2.5×10^{-5} mol L^{-1} base on monomeric units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
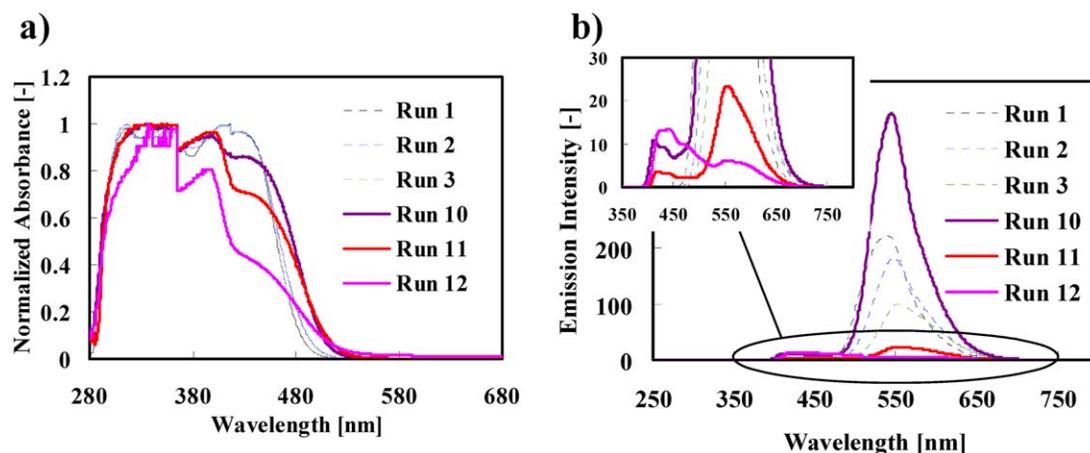
FIGURE 5 Normalized absorption (a) and emission (b) spectra of poly(CHMI-*co*-DHF) by Suzuki–Miyaura coupling reaction (Runs 10–12) and model compound (Runs 1–3 in Table 4) in various solvent (concentration; 2.5×10^{-5} mol L^{-1} base on monomeric units, inset, expanded emission spectra of Runs 10, 11). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wavelength for the other on the long wavelength region was smaller than the random copolymers by Yamamoto coupling reaction. By the slight difference, the emission colors observed by the naked eye significantly differed. The random copolymer showed white in *n*-hexane and magenta in THF in contrast to that one by Yamamoto coupling reaction exhibited yellow in *n*-hexane and orange in THF (Fig. 6, right).

While the alternating copolymer showed the bathochromic shift with increasing the polarity of solvent, an emission peak intensity of the random copolymers on the long wavelength region changed. The authors proposed the mechanism of this fluorescence solvatochromism of the random copolymers. At the first setout, the emissions of CHMI-DHF units in the polar solvent were probably quenched by the occurring rotation of the conjugated chains like an aggregation-induced emission

enhancement molecular.[55,56] To demonstrate this hypothesis, a PL spectrum in regard to the concentration change was measured in various solvents. The PL spectra of random copolymers by Yamamoto reaction (Table 2, Run 4) are shown in Figure 7. The measurements were carried out by the concentration of the polymer change from 2.5×10^{-5} to 2.5×10^{-7} mol L^{-1}. An emission peak intensity on the long wavelength region decreased with decreasing of the polymer concentration in *n*-hexane [Fig. 7(a)]. On the other hand, a peak intensity on the short wavelength region significantly increased in THF [Fig. 7(b)]. The peak intensity on the short wavelength region increased even in DMF [Fig. 7(c)]. These increases of the peak intensity on the part of the short wavelength with the concentration reduction were suggested to the moderation of concentration quenching. In addition, the peak intensity on the short wavelength region increased when the polymer concentration

TABLE 4 UV–Vis Absorption and PL Emission Spectral Data for Poly(CHMI-*co*-DHF) and Model Compound in Various Solvent[a]

Run	Reaction Name	Time (h)	Solv.	$\lambda_{abs.}$[b] (nm)	E.W.[c] (nm)	$\lambda_{Em.}$[d] (nm)
1	Model compound	–	*n*-Hexane	348, 416	416	540
2	Model compound	–	THF	317, 411	411	548
3	Model compound	–	DMF	313, 414	414	553
4	Yamamoto coupling	24	*n*-Hexane	303, 363	363	412, 546
5		24	THF	302, 365	365	418, 556
6		24	DMF	302, 365	365	421, 549
7		48	*n*-Hexane	303, 363	363	411, 546
8		48	THF	304, 363	363	418, 557
9		48	DMF	309, 364	364	421, 552
10	Suzuki–Miyaura coupling	48	*n*-Hexane	337, 398, 422	398	545
11		48	THF	338, 398, 433	398	420, 555
12		48	DMF	337, 396, 431	396	441, 555

[a] 2.5×10^{-5} mol L^{-1} based on monomeric units in various solvent.
[b] $\lambda_{abs.}$ = absorption peaks.
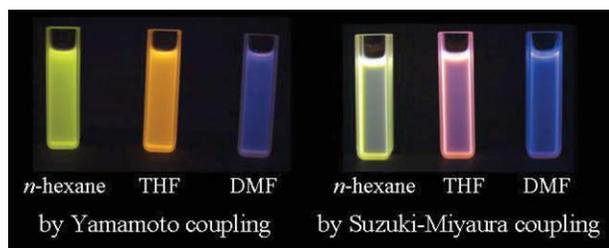[c] E.W. = excitation wavelength.
[d] $\lambda_{Em.}$ = emission peaks.

FIGURE 6 Photographs of poly(CHMI-*co*-DHF) by Yamamoto coupling reaction (left) and Suzuki–Miyaura coupling (right) under the UV light in various solvent (concentration; 2.5 × 10^{-5} mol L^{-1} base on monomeric units).

FIGURE 8 Emission spectra of poly(CHMI-*co*-DHF) by Suzuki–Miyaura coupling reaction (Run 7 in Table 2) by concentration change in *n*-hexane (concentration; from 2.5 × 10^{-5} to 2.5 × 10^{-7} mol L^{-1} base on monomeric units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was 2.5 × 10^{-7} M, but the intensity in regard to the long wavelength region decreased. The PL spectra of the random copolymer by Suzuki–Miyaura reaction (Table 2, Run 7) are shown in Figure 8. The copolymer showed the decreasing of the peak intensity on the long wavelength region and the increasing of the other on the short wavelength region with concentration reduction.

To additionally investigate the effect of Aggregation-Induced Emission Enhancement, PL spectra of a THF solution of copolymers adding MeOH as poor solvent (Table 2, Run 5) were measured (in Fig. 9). The authors expected that the peak
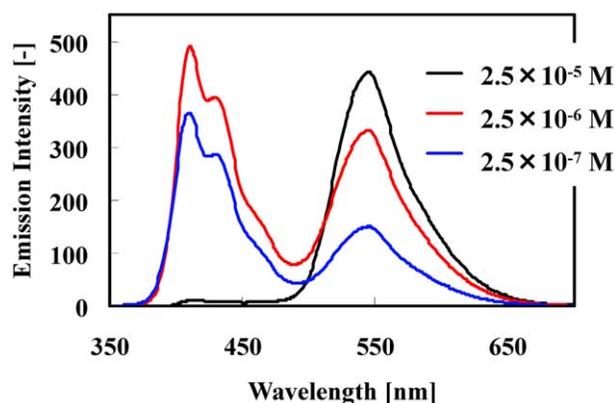
intensity on the long wavelength region attributed to CHMI-DHF would increase by the intermolecular aggregation. But the peak intensity was decreased and shown red shifts with increasing of MeOH. From these measurement results, it was indicated that the fluorescence solvatochromism was strongly attributed to not only the intermolecular aggregation but also
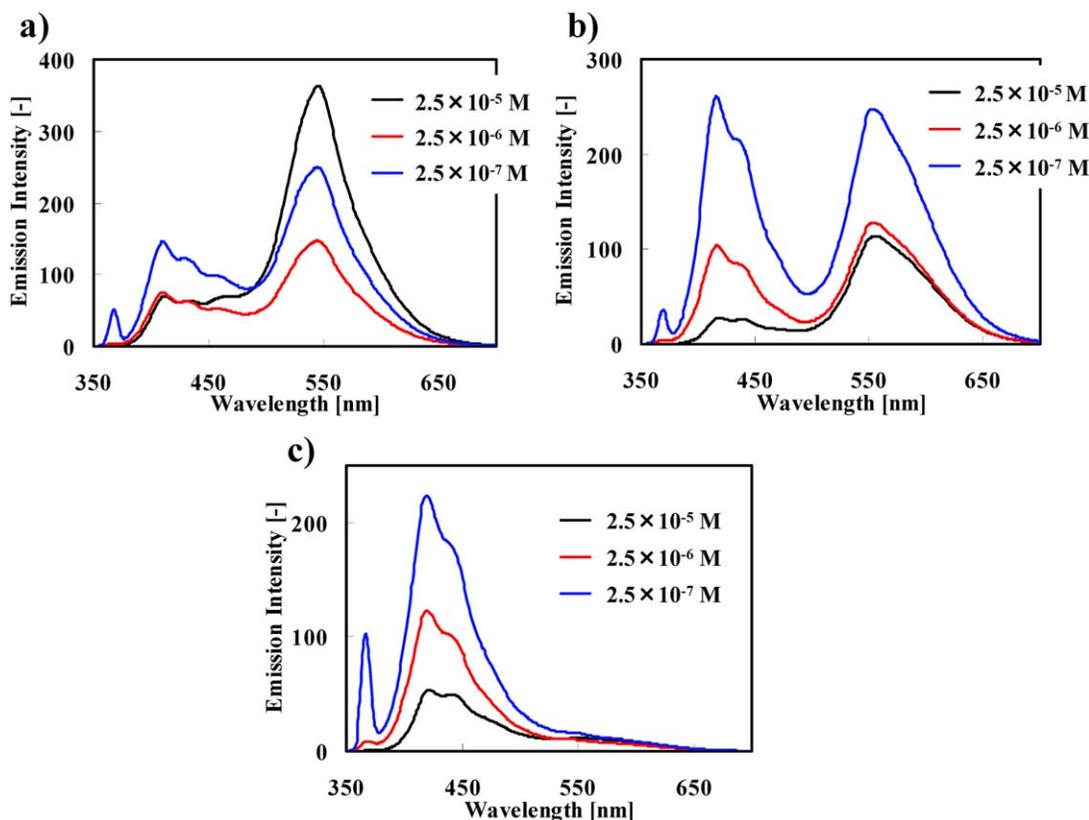

FIGURE 7 Emission spectra of poly(CHMI-*co*-DHF) by Yamamoto coupling reaction (Run 4 in Table 2) by concentration change in *n*-hexane (a), THF (b), and DMF (c) (concentration; from 2.5 × 10^{-5} to 2.5 × 10^{-7} mol L^{-1} base on monomeric units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
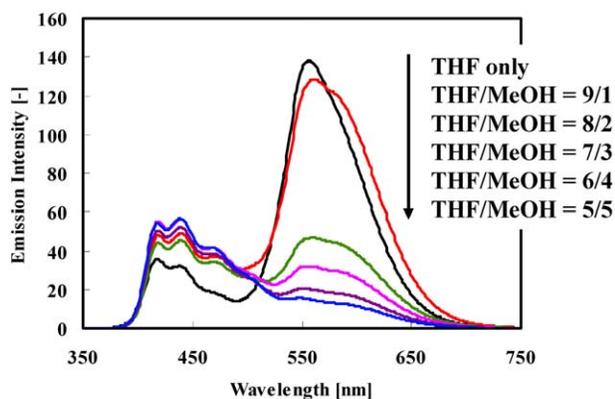
FIGURE 9 Emission spectra of poly(CHMI-*co*-DHF) by Yama-moto coupling reaction (Run 5 in Table 2) in mixed solvent of THF and MeOH (concentration; 2.5×10^{-5} mol L^{-1} base on monomeric units). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polarity of solvents. Therefore, the authors assumed that the fluorescence properties were attributed to twisted intramolecular charge transfer (TICT) states of CHMI-DHF units in excited state instead of aggregation induced emission enhancement. TICT was mainly observed with molecules having electron donor and acceptor units, for instance *p*-dimethylaminobenzonitrile as TICT molecule showed a dual fluorescence band in a polar solvent.[57] In excited state, TICT produced a new emission band and a red shift or quenching by twist between donor and acceptor units in polar solvents. Judging from the above measurement result, it was concluded that the fluorescence solvatochromism of copolymers was attributed to TICT states of CHMI-DHF units.

CONCLUSIONS

The authors prepared conjugated copolymers with *N*-cyclohexylmaleimide as an acceptor unit and 9,9-dihexylfluorene as a donor unit by Yamamoto coupling or Suzuki–Miyaura cross-coupling reaction. The copolymers could be obtained with moderate molecular weight ($M_n = 2600$–3500). The random copolymers showed two emission peaks on the parts of the short and long wavelength, respectively, and the emission colors observed by the naked eye were different by a difference of the each peak intensity. Furthermore, the alternating and random copolymers obtained in this article showed a difference fluorescence solvatochromism, respectively. In the alternating copolymer, the emission peak showed the red shift with increasing the polarity of solvent along with the model compound. On the other hand, the random copolymers showed the fluorescence solvatochromism by the change of two peak intensities. The PL spectra when the concentration of copolymers was changed or MeOH was added in THF solution of copolymer were measured. Judging from PL measurement results, the PL intensity on the long wavelength region attributed to CHMI-DHF bonding was affected by the polar solvent. These fluorescence properties might be attributed to TICT states of CHMI-DHF units in

excited state. This is why the authors could obtain the copolymers which showed various fluorescences by change of the polarity of the solvent.

REFERENCES AND NOTES

1 M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737–1750.

2 A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402–428.

3 J. M. Hancock, A. P. Gifford, Y. Zhu, Y. Lou, S. A. Jenekhe, *Chem. Mater.* **2006**, *18*, 4924–4932.

4 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539–541.

5 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121–128.

6 Y. Cao, I. D. Parker, G. Yu, C. Zhang, A. J. Heeger, *Nature* **1999**, *397*, 414–417.

7 S. H. Jin, M. Y. Kim, J. Y. Kim, K. Lee, Y. S. Gal, *J. Am. Chem. Soc.* **2004**, *126*, 2474–2480.

8 X. Zhang, D. M. Kale, S. A. Jenekhe, *Macromolecules* **2002**, *35*, 382–393.

9 Goel, M. Dixit, S. Chaurasia, A. Kumar, R. Raghunandan, P. R. Maulik, R. S. Anand, *Org. Lett.* **2008**, *10*, 2553–2556.

10 L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, J. D. Mackenzie, *Science* **2001**, *293*, 1119–1122.

11 Liscio, G. De Luca, F. Nolde, V. Palermo, K. Mcullen, P. Samori, *J. Am. Chem. Soc.* **2008**, *130*, 780–781.

12 C. Thompson, J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77.

13 Z. E. X. Dance, M. J. Ahrens, A. M. Vega, A. B. Ricks, D. W. McCamant, M. A. Ratner, M. R. Wasielewski, *J. Am. Chem. Soc.* **2008**, *130*, 830–832.

14 D. P. Hagberg, J.-H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, Md. K. Nazeeruddin, *J. Am. Chem. Soc.* **2008**, *130*, 6259–6266.

15 P. Gao, D. Beckmann, H. N. Tsao, X. Feng, V. Enkelmann, W. Pisula, K. Müllen, *Chem. Commun.* **2008**, 1548–1550.

16 H. Usta, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **2008**, *130*, 8580–8581.

17 C. Yang, J. Y. Kim, S. Cho, J. K. Lee, A. J. Heeger, F. Wudl, *J. Am. Chem. Soc.* **2008**, *130*, 6444–6450.

18 M. Palma, J. Levin, V. Lemaur, A. Liscio, V. Palermo, J. Cornil, Y. Geerts, M. Lehmann, Samori, P. *Adv. Mater.* **2006**, *18*, 3313–3317.

19 X. Chen, Y.-M. Jeon, J.-W. Jang, L. Qin, F. Huo, W. Wei, C. A. Mirkin, *J. Am. Chem. Soc.* **2008**, *130*, 8166–8168.

20 T.-L. Coi, K.-H. Lee, W.-J. Joo, S. Lee, T.-W. Lee, M. Y. Chae, *J. Am. Chem. Soc.* **2007**, *129*, 9842–9843.

21 M. Grell, W. Knoll, D. Lupo, A. Meisel, T. Miteva, D. Neher, H.-G. Nothofer, U. Scherf, A. Yasuda, *Adv. Mater.* **1999**, *11*, 671–675.

22 U. Scherf, E. J. List, W. *Adv. Mater.* **2002**, *14*, 477–487.

23 W. Yu, J. Pei, W. Huang, A. J. Heeger, *Adv. Mater.* **2000**, *12*, 828–831.

24 P. Herguth, X. Jiang, M. S. Liu, A. K. Y. Jen, *Macromolecules* **2002**, *35*, 6094–6100.

25 J. Lee, H. J. Cho, B. J. Jung, N. S. Cho, H. K. Shim, *Macromolecules* **2004**, *37*, 8523–8529.

26 N. S. Cho, J. H. Park, S. K. Lee, J. Lee, H. K. Shim, M. J. Park, D. H. Hwang, B. J. Jung, *Macromolecules* **2006**, *39*, 177–183.

27 P. Kulkarni, X. Kong, S. A. Jenekhe, *Macromolecules* **2006**, *39*, 8699–8711.

28 M. J. Park, J. Lee, J. H. Park, S. K. Lee, J. I. Lee, H. Y. Chu, D. H. Hwang, H. K. Shim, *Macromolecules* **2008**, *41*, 3063–3070.

29 E. Lim, B.-J. Jung, H. K. Shim, *Macromolecules* **2003**, *36*, 4288–4293.

30 S. Liu, H. S. O. Chan, S. C. Ng, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 4792–4801.

31 J. Yang, C. Jiang, Y. Zhang, R. Yang, W. Yang, Q. Hou, Y. Cao, *Macromolecules* **2004**, *37*, 1211–1218.

32 P. Kulkarni, Y. Zhu, S. A. Jenekhe, *Macromolecules* **2005**, *38*, 1553–1563.

33 W.-C. Wu, C.-L. Liu, W.-C. Chen, *Polymer* **2006**, *47*, 527–538.

34 S. T. Huang, D. J. Liaw, L. G. Hsieh, C. C. Chang, M. K. Leung, K. L. Wang, W. T. Chen, K. R. Lee, J. Y. Lai, L. H. Chan, C. T. Chen, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 6231–6245.

35 W.-C. Wu, W.-Y. Lee, W.-Ch. Chen, *Macromol. Chem. Phys.* **2006**, *207*, 1131–1138.

36 Tsami, X.-H. Yang, F. Galbrecht, T. Farrell, H. S. Adamczyk, R. Heiderhoff, L. J. Balk, D. Neher, E. Holder, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 4773–4785.

37 H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, *Nature* **2000**, *404*, 478–481.

38 P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, W. Andreoni, *Appl. Phys. Lett.* **2002**, *80*, 2517–2519.

39 K. N. N. Unni, A. K. Pandey, J.-M. Nunzi, *Chem. Phys. Lett.* **2005**, *407*, 95–99.

40 H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, A. Dodabalapur, *Nature* **2000**, *404*, 478–481.

41 H. Z. Chen, M.-M. Shi, T. Aernouts, M. Wang, G. Borghs, P. Heremans, *Sol. Energy Mater. Sol. Cells* **2005**, *87*, 521–527.

42 B. K. Kaletas, R. M. Williams, B. König, L. De Cola, *Chem. Commun.* **2002**, 776–777.

43 L.-H. Chan, Y.-D. Lee, C.-T. Chen, *Macromolecules* **2006**, *39*, 3262–3269.

44 N. C. Yang, D. H. Suh, *Macromol. Rapid Commun.* **2001**, *22*, 335–338.

45 N. C. Yang, D. H. Suh, *Polymer* **2001**, *42*, 7987–7992.

46 R.-H. Lee, L.-Y. Lee, *Colloid Polym. Sci.* **2011**, *289*, 1215–1231. (a) K. Onimura, M. Matsushima, K. Yamabuki, T. Oishi, *Polym. J.* **2010**, *42*, 290–297; (b) K. Onimura, Matsushima, M. Nakamura, T. Tominaga, K. Yamabuki, T. Oishi, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3550–3558; (c) K. Onimura, M. Nakamura, K. Amatsu, M. Matsushima, K. Yamabuki, T. Oishi, *Chem. Lett.* **2013**, *42*, 366–368.

47 M. Dubernet, V. Caubert, J. Guillard, M.-C. Viaud-Massuard, *Tetrahedron* **2005**, *61*, 4585–4593.

48 H.-C. Lin, K.-W. Lee, C.-M. Tsai, K.-H. Wei, *Macromolecules* **2006**, *39*, 3808–3816.

49 B. Nowacki, E. Iamazaki, A. Cirpan, F. Karasz, T. D. Z. Atvars, L. Akcelrud, *Polymer* **2009**, *50*, 6057–6064.

50 G. Hughes, C. Wang, A. Batsanov, M. Fern, S. Frank, M. R. Bryce, I. F. Perepichka, A. P. Monkman, B. P. Lyons, *Org. Biomol. Chem.* **2003**, *1*, 3069–3077.

51 S.-J. Liu, Q. Zhao, R.-F. Chen, Y. Deng, Q.-L. Fan, F.-Y. Li, L.-H. Wang, C.-H. Huang, W. Huang, *Chem. Eur. J.* **2006**, *12*, 4351–4361.

52 H. Wang, G. Chen, Y. Liu, L. Hu, X. Xu, S. Ji, *Dyes Pigments* **2009**, *83*, 269–275.

53 Z.-B. Zhang, M. Fujiki, H.-Z. Tang, M. Motonaga, K. Torimitu, *Macromolecules* **2002**, *35*, 1988–1990.

54 H. Tong, Y. Hong, Y. Dong, M. Häussler, Z. Li, J. W. Y. Lam, Y. Dong, H. H.-Y. Sung, I. D. Williams, B. Z. Tang, *J. Phys. Chem. B* **2007**, *111*, 11817–11823.

55 Y. Hong, H. Xiong, J. W. Y. Lam, M. Häußler, J. Liu, Y. Yu, Y. Zhong, H. H. Y. Sung, I. D. Williams, K. S. Wong, B. Z. Tang, *Chem. Eur. J.* **2010**, *16*, 1232–1245.

56 Z. R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.* **2003**, *103*, 3899–4031.