



## Synthesis of conjugated polymers via direct C H/C Cl coupling reactions using a Pd/Cu binary catalytic system

著者 (英)	Junpei KUWABARA, Wataru Tsuchida, Shuyang Guo, Ziwei Hu, Takeshi Yasuda, Takaki KANBARA
journal or publication title	Polymer Chemistry
volume	10
number	18
page range	2298-2304
year	2019-05
URL	<a href="http://hdl.handle.net/2241/00159475">http://hdl.handle.net/2241/00159475</a>

doi: 10.1039/C9PY00232D

## ARTICLE

# Synthesis of Conjugated Polymers via Direct C–H/C–Cl Coupling Reactions Using a Pd/Cu Binary Catalytic System

Junpei Kuwabara,<sup>\*a</sup> Wataru Tsuchida,<sup>a</sup> Shuyang Guo,<sup>a</sup> Ziwei Hu,<sup>a</sup> Takeshi Yasuda,<sup>b</sup> Takaki Kanbara<sup>\*a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

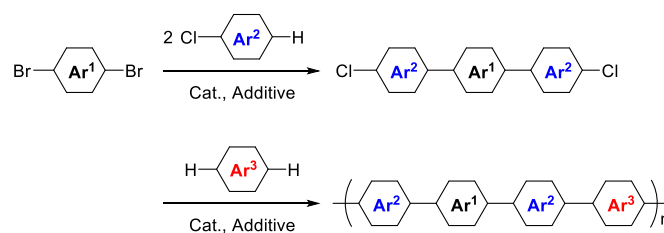
DOI: 10.1039/x0xx00000x

Direct arylation polycondensation is regarded as an efficient synthetic method for conjugated polymers. This methodology is difficult to apply to dichloroaryl monomers because of the low reactivity of C–Cl bonds compared to that of the C–Br bonds in dibromoaryl monomers, which have been widely used in direct arylation polycondensation. In this research, direct arylation polycondensation of dichloroaryl monomers was achieved by use of a Pd/Cu binary catalytic system. Optimisation of the molar ratio of the Pd and Cu catalyst resulted in the formation of high-molecular-weight polymers in good yields. Structural defects of the polymer at the terminal unit were minimised by logical choice of the monomer ratio on the basis of the reaction mechanism. The obtained polymer with relatively low structural defects showed higher quantum efficiency of photoluminescence and electroluminescence than that of the polymer with irregular terminal structures.

## Introduction

In recent years, polycondensation through C–H direct arylation reactions has been developed as an efficient synthetic method for conjugated polymers because it has the advantages of a shorter monomer synthesis and a smaller amount of by-products than those of traditional methods with conventional cross-coupling reactions.<sup>1–6</sup> Direct arylation polycondensation under optimised conditions affords conjugated polymer materials of high quality in terms of high molecular weight and purity. These high-quality polymers show good performance in organic optoelectronic devices, such as organic photovoltaics and organic field-effect transistors.<sup>7–9</sup> In the direct arylation polycondensation, C–H/C–Br coupling reactions have mainly been used for C–C bond formations.<sup>10–13</sup> Development of polycondensation through direct C–H/C–Cl coupling reactions enables the substrate scope to be expanded to dichloroaryl monomers. The use of dichloroaryl monomers generally reduces the cost of the monomers. In addition, development of the direct C–H/C–Cl coupling polycondensation provides new efficient synthetic routes for conjugated polymers by monomer synthesis with selective C–H/C–Br coupling<sup>14</sup> and polycondensation with C–H/C–Cl coupling (Scheme 1). Achievement of this strategy requires efficient C–H/C–Cl coupling reactions, which are much more difficult than C–H/C–Br coupling reactions.<sup>15</sup> In direct C–H/C–Cl coupling, the catalyst needs to cleave strong C–Cl bonds. In cases with Pd catalysts, strong electron-donating ligands, such as P(*t*-Bu)<sub>3</sub> and *N*-heterocyclic carbene (NHC) ligands, are required to promote

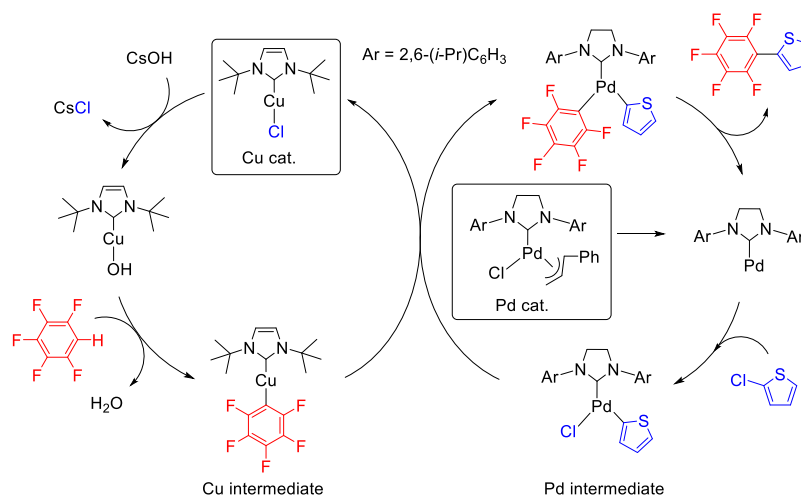
oxidative addition to the C–Cl bonds.<sup>16,17</sup> However, these electron-rich Pd catalysts cannot efficiently promote C–H bond cleavage via a concerted metallation–deprotonation (CMD) process, presumably because the weak electrophilic nature of the Pd centre results in a weak Pd–C interaction in the CMD transition state.<sup>18,19</sup> Owing to this trade-off, Pd-catalysed direct C–H/C–Cl coupling reactions require harsh conditions and/or special tricks.<sup>20–25</sup> Mori and co-workers reported direct arylation of benzothiophene with 4-chlorotoluene by using a strong base (LiOt-Bu) with Pd[P(*t*-Bu)<sub>3</sub>]<sub>2</sub> catalyst.<sup>26</sup> Recently, binary catalytic systems have been reported in direct C–H/C–Cl coupling reactions. Cazin and co-workers reported a Pd/Cu binary catalytic system, in which the Pd catalyst with an NHC ligand promotes C–Cl bond cleavage and the Cu catalyst promotes C–H bond cleavage (Scheme 2).<sup>27</sup> A transmetalation reaction affords a Pd–biaryl intermediate that generates a cross-coupling product via reductive elimination. This cooperative effect achieved highly efficient C–H/C–Cl coupling reactions. In this research, we focus on the binary catalytic system for direct arylation polycondensation of dichloroaryl monomers. Optimisation of the reaction conditions enabled the production of high-molecular-weight polymers with minimal defect structures. The relationships between the defect structures and material performances in organic light-emitting diodes (OLEDs) are discussed to highlight the importance of accurate polymerisation methods in material synthesis.



Scheme 1. Stepwise direct arylation of bromoaryl and chloroaryl for synthesis of conjugated polymers.

<sup>a</sup> Tsukuba Research Center for Energy Materials Science (TREMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.

<sup>b</sup> Research Center for Functional Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.  
Electronic Supplementary Information (ESI) available See Electronic Supplementary Information (ESI) available See DOI: 10.1039/x0xx00000x



Scheme 2. Reaction mechanism of cooperative catalytic system.

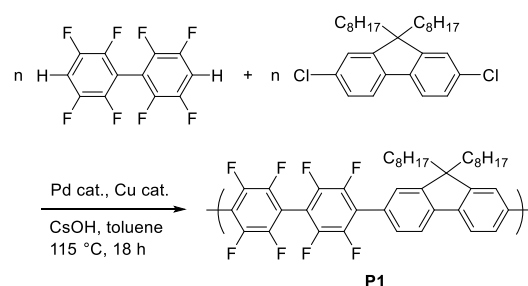
## Results and discussion

### Polycondensation with dichlorofluorene monomer

The reaction of octafluorobiphenyl with 2,7-dichloro-9,9-di-*n*-octylfluorene was selected as a model reaction for the direct C–H/C–Cl coupling polycondensation (Table 1) because of the high reactivity of the C–H bond in octafluorobiphenyl and sufficient solubility of the polymer (P1). P1 has been previously synthesised via direct arylation polycondensation of octafluorobiphenyl with 2,7-dibromo-9,9-di-*n*-octylfluorene.<sup>28</sup> The reaction with the dibromofluorene monomer afforded P1 with a molecular weight of 43,200 in 95% yield, whereas the reaction with 2,7-dichloro-9,9-di-*n*-octylfluorene under the same reaction conditions did not afford a polymeric product (Scheme S1). This is associated with the low reactivity of C–Cl bonds relative to that of C–Br bonds. On the basis of the report by Cazin et al.,<sup>27</sup> the Pd/Cu binary catalytic system was then applied to the reaction (Table 1). The reaction with 5 mol% of the Pd and Cu catalysts afforded a polymer in low yield (Table 1, Entry 1). Structural analysis of the polymer by matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF MS) reveals the presence of C–Cl/C–Cl homo-coupling defects in the polymer (Figure S1). From the viewpoint of the reaction mechanism, C–Cl/C–Cl homo-coupling defects might be produced from the Pd intermediate before transmetalation with the Cu intermediate (Scheme S2).<sup>29–31</sup> To suppress this side reaction of the Pd intermediate, the molar ratio of the Cu catalyst was increased, as shown in Table 1, Entries 2–4. The reaction with 2.5 mol% of the Pd catalyst and 10 mol% of the Cu catalyst gave the highest molecular weight and yield (Table 1, Entry 3); this is the best ratio for this polymerisation. Structural analysis of the obtained polymer showed no structural defects, including homo-coupling defects and ligand incorporation at the terminal units (Figure S1–S3). The results of an elemental analysis also support the repeating structure and prove the purity of the polymer. The catalyst ratio of Pd:Cu = 1:10 afforded a polymer containing C–H/C–H homo-coupling defects (Table 1, Entry 4); an excess amount of the Cu catalyst

results in a side reaction of the Cu intermediate (Scheme S2).<sup>32</sup> The model reactions with the dichlorofluorene monomer showed the importance of a molar ratio of the catalysts to keep balance of Pd and Cu catalysis. The well-balanced ratio enables to promote the desired transmetalation reaction of the each intermediate, and to suppress the side reactions or decomposition.<sup>33,34</sup>

**Table 1 Results of polycondensation reactions with various molar ratios of the catalysts**

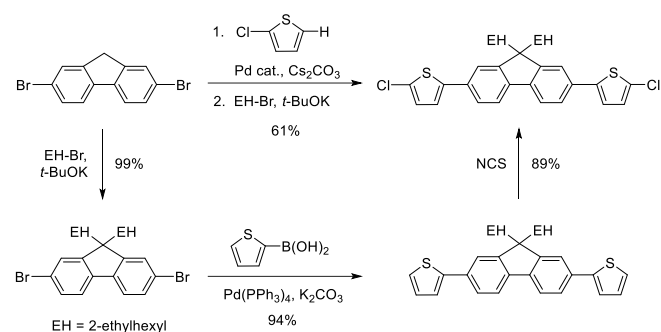


Entry	Pd cat. (mol%)	Cu cat. (mol%)	Yield (%)	$M_n^c$	$M_w/M_n^c$
1	5.0	5.0	24 <sup>a</sup>	22,700	1.6
2	5.0	10	59	43,900	1.9
3	2.5	10	87	57,600	2.6
4	1.0	10	77 <sup>b</sup>	46,600	2.1

<sup>a</sup> C–Cl/C–Cl homo-coupling defects were included. <sup>b</sup> C–H/C–H homo-coupling defects were included. <sup>c</sup> Estimated by Gel Permeation Chromatography (GPC) calibrated with polystyrene standards and with CHCl<sub>3</sub> as the eluent at 40 °C.

### Synthesis of three-component polymer via C–H/C–Br and C–H/C–Cl coupling reaction

To prove the advantages of this synthetic strategy, the next target involved the synthesis of a conjugated polymer bearing three kinds of unit. As illustrated in Scheme 1, the monomer was prepared by selective C–H/C–Br coupling, and the polycondensation was conducted by C–H/C–Cl coupling. The designed monomer was prepared by a direct arylation reaction of 2-chlorothiophene with 2,7-dibromofluorene<sup>4</sup> and subsequent introduction of alkyl chains in a one-pot, two-step fashion (Scheme 3). The same monomer can also be prepared by a conventional stepwise method, namely the introduction of the alkyl chains, the Suzuki–Miyaura coupling reaction, and a chlorination reaction. Although the yield of the one-pot method (61%) was lower than the total yield of the conventional three-step reaction (83%), the target monomer was obtained via a simple reaction from easily available compounds and one purification step.

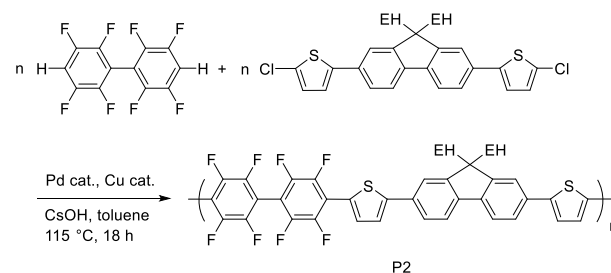


Scheme 3. Monomer synthesis via the direct C–H/C–Br coupling reaction.

The results of the direct C–H/C–Cl polycondensation are summarised in Table 2. At first, the reaction was conducted under the optimised conditions for the aforementioned dichlorofluorene monomer, which afforded the corresponding polymer with moderate molecular weight and yield (Table 2, Entry 1). The MALDI-TOF mass spectrum showed that the polymer contains terminal defects involving the carbene ligand that originates from the Pd catalyst (Figure S6). The terminal unit should be caused by decomposition of the Pd intermediate (Scheme S2).<sup>35,36</sup> An increase in Cu catalyst loading improved the yield and molecular weight (Table 2, Entries 2–4). The increased amount of the Cu catalyst might accelerate the desired reaction over decomposition of the Pd intermediate. Figure 1a shows the <sup>1</sup>H NMR spectrum of the polymer described in Table 2, Entry 3 (P2-3). Each signal was assigned to the repeating unit, and the integral ratios of the signals agree with the assignments. However, the MALDI-TOF mass spectrum of P2-3 shows the presence of terminal defects with the decomposed carbene ligand (Figure S6). Although the mass spectra indicate that all of the polymers have terminal defects, this is considered to be an overestimation, judging from the results of the <sup>1</sup>H NMR analysis. This mismatch is presumably caused by high sensitivity to the polymers with the cationic terminal unit in mass spectrometry. The <sup>19</sup>F NMR spectrum of P2-3 exhibits unknown minor signals with low intensity, in addition to signals for the repeating units and the octafluorobiphenyl terminal unit (Figure 1c). To suppress the minor structural defects, a reaction was conducted at lower temperature (100 °C), but this gave only oligomeric products

(Table 2, Entry 5). The use of a slight excess of octafluorobiphenyl (1.03 equivalents) was then tested (Table 2, Entry 6) because a shortage of the octafluorobiphenyl terminal could result in decomposition of the Pd intermediate at a late stage of the polycondensation reaction (Scheme S2). The yield and molecular weight of the polymer described in Table 2, Entry 6 (P2-6) are comparable with those for the polymer described in Table 2, Entry 2; therefore, the non-equivalent monomer ratio did not decrease the degree of polymerisation. The <sup>1</sup>H NMR spectrum of P2-6 shows the presence of the octafluorobiphenyl and dechlorinated thiophene terminal units (Figure 1b, Figure S7). The <sup>19</sup>F NMR spectrum also indicates that the structure has minimal defects (Figure 1d); the spectrum exclusively exhibits the signals of the repeating unit and octafluorobiphenyl terminal unit. In addition, the results of elemental analysis of the polymer agree with the calculated values of the repeating units (Table S1). In the MALDI-TOF mass spectrum of P2-6, no peak was detected for the polymer, presumably due to difficulties in the vapourisation and ionisation processes of the neutral polymer without terminal defects. This agrees with the fact that the neutral polymer has not been observed in the other spectra (Figure S6). Comprehensive data from NMR, elemental analysis, and MALDI-TOF mass support the less defect of P2-6 in comparison with P2-3.

Table 2 Results of direct arylation polycondensation of the chlorothiophenyl monomer



Entry	Pd cat. (mol%)	Cu cat. (mol%)	Yield (%)	$M_n^c$	$M_w/M_n^c$
1	2.5	10	54	5,300 <sup>d</sup>	1.6 <sup>d</sup>
2	2.5	15	84	21,800	2.8
3	2.5	20	78	27,000	3.1
4	2.5	25	80	23,900	2.8
5 <sup>a</sup>	2.5	15	4	3,700 <sup>d</sup>	1.1 <sup>d</sup>
6 <sup>b</sup>	2.5	15	91	20,100	2.2

<sup>a</sup> Reaction at 100 °C. <sup>b</sup> 1.03 equivalents of octafluorobiphenyl were used. <sup>c</sup> Estimated by GPC calibrated with polystyrene standards and with *o*-dichlorobenzene as the eluent at 140 °C. <sup>d</sup> Estimated by GPC calibrated with polystyrene standards and with CHCl<sub>3</sub> as the eluent at 40 °C.

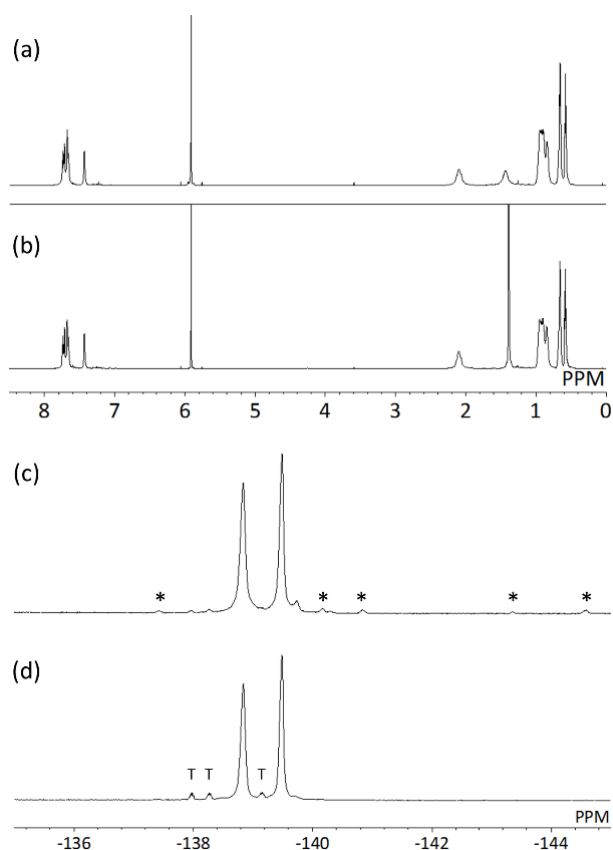


Figure 1.  $^1\text{H}$  NMR spectra of (a) P2-3 (Table 2, Entry 3) and (b) P2-6 (Table 2, Entry 6) (600 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K);  $^{19}\text{F}$  NMR spectra of (c) P2-3 and (d) P2-6 (564 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K). T denotes the signals of the octafluorobiphenyl terminal units. Signals with asterisks were associated with irregular structures.

### Physical properties

The photoluminescence (PL) and electroluminescence (EL) properties of the polymer were evaluated to investigate the effects of the structural accuracy on the physical properties. The polymers from Entry 3 (P2-3) and Entry 6 (P2-6) in Table 2 were selected as representative samples of defect and no defect structures, respectively. These polymers have similar absorption properties, HOMO/LUMO energy levels, and surface roughness in the thin-film state (Table S2, Figures S10 and S11). These data show that the terminal defects in P2-3 do not affect these physical properties. In contrast, the PL quantum yields ( $\Phi$ ) of P2-3 are lower than those of P2-6 (Table 3). This trend is particularly clear in the film state. The terminal defects are considered to induce quenching of PL, which is more pronounced in the condensed solid state. In addition, the EL properties of these two polymers were evaluated in OLED devices. The EL spectrum was similar to the PL spectrum in each case (Figure 2a, Figure S12). The maximal external quantum efficiency (EQE) of the OLED with P2-6 was higher than that of the OLED with P2-3, which reflects the high PL quantum yield of the high-quality polymer P2-6 (Figure 2b and Table 3). These PL and EL properties emphasise the importance of the structural accuracy of the polymer materials. We have reported low OLED performance of a polymer with

other terminal defects that originate from phosphine ligands.<sup>37</sup> The improved device structure with poly(9-vinylcarbazole) as an electron blocking material reached  $3037 \text{ cd m}^{-2}$  at a current of  $343.6 \text{ mA cm}^{-2}$ , and the EQE of the OLED was 0.75% at  $10.6 \text{ mA cm}^{-2}$  (Figure S14).

Table 3. Photoluminescence and electroluminescence properties of P2

	PL (Solution)		PL (Film)		EL	
	$\lambda_{\text{em}}$ (nm)	$\Phi$ (%)	$\lambda_{\text{em}}$ (nm)	$\Phi$ (%)	$\lambda_{\text{em}}$ (nm)	EQE (%)
P2-3 <sup>a</sup>	460	55	496	5	498	0.11
P2-6 <sup>b</sup>	457	71	496	19	494	0.45

<sup>a</sup>The polymer from Entry 3 in Table 2. <sup>b</sup>The polymer from Entry 6 in Table 2.

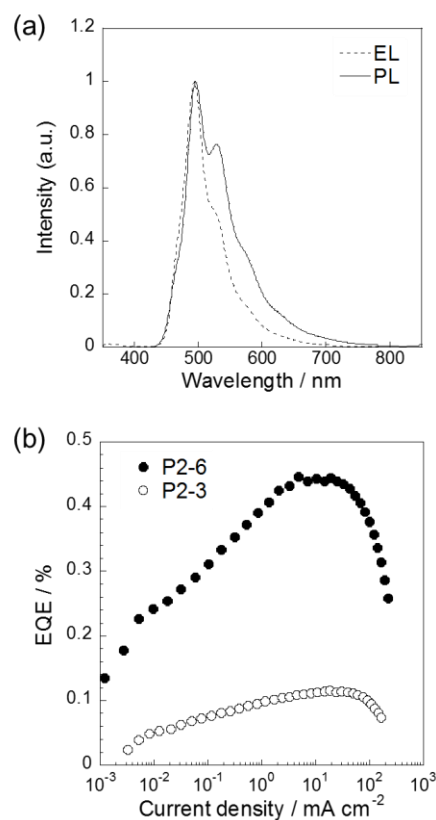


Figure 2. (a) PL and EL spectra of the OLEDs with P2-6 at 8 V. (b) EQEs of the OLEDs. Configuration ITO/PEDOT:PSS(40 nm)/P2-3(48 nm) or P2-6(48 nm)/TPBi(40 nm)/LiF(1 nm)/Al(100 nm)

### Conclusions

Direct arylation polycondensation of dichloroaryl monomers was demonstrated with a Pd/Cu binary catalytic system that promoted efficient C–H/C–Cl coupling reactions. Optimisation of the reaction conditions, especially the molar ratio of the Pd and Cu catalyst, resulted in the formation of high-molecular-

weight polymers in good yields from dichloroaryl monomers combined with octafluorobiphenyl monomers. Structural defects of the polymer at the terminal unit were minimised by logical choice of the monomer ratio on the basis of the reaction mechanism. The obtained pure polymer with minimal defects showed higher quantum efficiency of photoluminescence and electroluminescence than that of the polymer with irregular terminal structures. These results clarify the importance of the terminal unit in luminescence applications. This research provides an efficient synthetic route to conjugated polymers with the high quality that is essential for organic electronic devices. This methodology will provide high-performance semiconducting materials by the combination of other fluorinated monomers and dichloroaryl monomers in short synthetic steps.

## Experimental

### Materials

All of the chemicals were used as received unless noted. All of the general organic solvents were purchased from Kanto Chemical. CuCl and Pd cat. ([Pd(SIPr)(cin)Cl]) were purchased from Wako Pure Chemical Industries and stored in a glove box. 2,7-Dibromofluorene, 2,2',3,3',5,5',6,6'-octafluorobiphenyl, and 2-chlorothiophene were purchased from Tokyo Chemical Industries (TCI). Cesium hydroxide was purchased from Sigma-Aldrich.  $\text{CDCl}_3$  and 1,1,2,2-Tetrachloroethane- $d_2$  were purchased from Acros Organics. 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenylbenzimidazole) (TPBi) was purchased from Luminescence Technology Corp. 2,7-Dichloro-9,9-dioctylfluorene<sup>38</sup> and Cu cat. ([1,3-di-*tert*-butyl-imidazol-2-ylidene]chloro-copper(I))<sup>39</sup> were prepared according to previously reported methods.

### General Methods

$^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AVANCE-400 or AVANCE-600 Spectrometer at 22 °C unless noted. Gel permeation chromatography (GPC) measurements were carried out on a Shimadzu prominence GPC system equipped with polystyrene gel columns using chloroform as an eluent at 40 °C after calibration with polystyrene standards. High-temperature GPC measurements were carried out using a HLC-8321 GPC/HT (TOSOH) using *o*-dichlorobenzene as the eluent after calibration with polystyrene standards (140 °C). Elemental analyses were carried out with a Perkin-Elmer 2400-CHN instrument. MALDI-TOF-MS data were recorded on AB SCIEX MALDI TOF/TOF 5800 using DCBT (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix. Air sensitive reactions were carried out in a Schlenk tube using a standard Schlenk technique or in a glove box manufactured by Miwa. Ultraviolet visible absorption spectra of the spin coated thin films were recorded on a Hitachi U-3010 spectrophotometer. Photoluminescence spectra were recorded on a Jasco FP-6500 spectrofluorometer. The HOMO energy level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer.

### Synthesis of P1 (Table 1, Entry 3)

2,7-Dichloro-9,9-dioctylfluorene (115 mg, 0.25 mmol), 2,2',3,3',4,4',5,5'-octafluorobiphenyl (74.5 mg, 0.25 mmol), and Cu cat. (7.0 mg, 25  $\mu\text{mol}$ ) were added to a 25 mL Schlenk tube. After degassing and filling with  $\text{N}_2$ , Pd cat. (4.1 mg, 6.3  $\mu\text{mol}$ ), CsOH (97.4 mg, 0.65 mmol), and toluene (1.25 mL) were added in a glove box. The mixture was stirred at 115 °C for 18 h under a  $\text{N}_2$  atmosphere. After cooling to room temperature, an aqueous solution of sodium diethyldithiocarbamate (0.1 M) was added and stirred overnight. The organic phase was separated and washed with water. The solution was concentrated and reprecipitated into methanol. The precipitates were collected by filtration, washed with hexane, and dried under reduced pressure. P1 was isolated as a pale yellow solid in 87% yield.  $M_n = 57600$ ,  $M_w/M_n = 2.6$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (br d, 2H), 7.59 (br s, 4H), 2.06 (br, 4H), 1.21-1.12 (m, 20H), 0.826 (m, 10H). The spectral data are essentially same as the reported data.<sup>28</sup> Elemental Analysis: Calculated for  $\text{C}_{35}\text{H}_{44}\text{N}_2\text{S}_2$ : C, 71.92; H, 5.89. Found: C, 72.01, H, 6.06.

### Synthesis of 2,7-bis-(5-chloro-thiophene-2-yl)-9,9-bis-(2-ethylhexyl)fluorene

2,7-Dibromofluorene (324 mg, 1.0 mmol), 1-adamantanecarboxylic acid (180 mg, 1.0 mmol), 2-chlorothiophene (0.46 mL, 5.0 mmol), and tris(2-methoxyphenyl)phosphine (35.2 mg, 0.10 mmol) were added to a 25 mL Schlenk tube. After degassing and filling with  $\text{N}_2$  gas,  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (26 mg, 0.025 mmol),  $\text{Cs}_2\text{CO}_3$  (1.00 g, 3.1 mmol), and toluene (10 mL) were added in a glove box. The mixture was stirred at 100 °C for 24 h under a  $\text{N}_2$  atmosphere. After cooling to room temperature, 1-bromo-2-ethylhexane (392  $\mu\text{L}$ , 2.2 mmol), potassium *tert*-butoxide (280 mg, 2.5 mmol), and THF (10 mL) were added to the reaction mixture. After stirring at 40 °C for 18 h under a  $\text{N}_2$  atmosphere, water and  $\text{CHCl}_3$  were added. The organic phase was separated, washed with water, and dried with  $\text{Na}_2\text{SO}_4$ . Purification by column chromatography (silica gel,  $\text{CHCl}_3$ :hexane = 1:19) afforded 2,7-bis-(5-chloro-thiophene-2-yl)-9,9-bis-(2-ethylhexyl)fluorene as a yellow solid (381 mg, 61 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (d,  $J = 8.4$  Hz, 2H), 7.49-7.47 (m, 4H), 7.09 (m, 2H), 6.90 (d,  $J = 4.0$  Hz, 2H), 2.07-1.97 (m, 4H), 0.95-0.47 (m, 30H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 151.54, 143.73, 140.55, 132.13, 128.77, 127.14, 124.64, 121.90, 121.16, 120.19, 55.08, 44.35, 34.74, 33.87, 28.16, 27.15, 22.71, 13.93, 10.36. Elemental Analysis: Calculated for  $\text{C}_{37}\text{H}_{44}\text{Cl}_2\text{S}_2$ : C, 71.24; H, 7.11. Found: C, 71.20, H, 7.26.

### Synthesis of P2 (Table 2, Entry 6)

2,7-Bis-(5-chloro-thiophene-2-yl)-9,9-bis-(2-ethylhexyl)fluorene (156 mg, 0.250 mmol) and 2,2',3,3',4,4',5,5'-octafluorobiphenyl (76.7 mg, 0.258 mmol) were added to a 25 mL Schlenk tube. After degassing and filling with  $\text{N}_2$ , Pd cat. (4.1 mg, 6.3  $\mu\text{mol}$ ), Cu cat. (10.5 mg, 38  $\mu\text{mol}$ ), CsOH (97.4 mg, 0.65 mmol), and toluene (1.25 mL) were added to the Schlenk tube in a glove box. The mixture was stirred at 115 °C for 18 h under a  $\text{N}_2$  atmosphere. After cooling to room

temperature, an aqueous solution of sodium diethyldithiocarbamate (0.1 M) and  $\text{CHCl}_3$  were added and stirred for several hours. The organic phase was separated and washed with water. The solution was concentrated and reprecipitated into methanol. The precipitates were collected by filtration, washed with hexane, and dried under reduced pressure. P2 was isolated as a pale yellow solid in 91% yield.  $M_n = 20100$ ,  $M_w/M_n = 2.2$ .  $^1\text{H}$  NMR (600 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K):  $\delta$  7.70 (br m, 4H), 7.43 (s, 1H), 2.10 (br s, 2H), 0.95–0.53 (m, 15H).  $^{19}\text{F}$  NMR (564 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K): -138.82, -139.48.  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 373 K): 151.83, 148.95, 144.66 (dd,  $J_{\text{C-F}} = 249$ , 15 Hz), 143.62 (d  $J_{\text{C-F}} = 251$  Hz), 141.01, 131.96, 131.96 (overlap), 126.13, 125.28, 123.18, 121.88, 120.19, 116.41, 104.57, 55.24, 44.75, 35.15, 34.12, 28.35, 27.29, 22.48, 13.51, 10.24. Calculated for  $\text{C}_{35}\text{H}_{44}\text{N}_2\text{S}_2$ : C, 69.32; H, 5.22. Found: C, 68.96, H, 5.10.

### Fabrication and characterization of OLEDs

OLEDs were fabricated in the following configuration: ITO/PEDOT:PSS/light emitting layer (P2)/electron transporting and hole blocking layer (TPBi)/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10  $\Omega$ /square) was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110  $^\circ\text{C}$  for 10 min on a hot plate. The substrate was then transferred to a  $\text{N}_2$ -filled glove box where it was re-dried at 110  $^\circ\text{C}$  for 10 min on a hot plate. A chloroform solution of P2-6 (4 mg/1 mL) was subsequently spin-coated onto the PEDOT:PSS surface to form the light emitting layer (48 nm). TPBi (40 nm), LiF (1 nm) and Al (100 nm) were then deposited onto the active layer with conventional thermal evaporation at a chamber pressure lower than  $5 \times 10^{-4}$  Pa, which provided the devices with an active area of  $2 \times 2$  mm<sup>2</sup>. Current-voltage characteristics and luminance of the OLED were simultaneously measured using an ADCMT 6246 DC voltage current source/monitor (ADC CORPORATION) and an LS-100 luminance meter (KONICA MINOLTA JAPAN, INC.), respectively. The EL spectra and the coordinates of the CIE chromaticity were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.).

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

The authors thank the Chemical Analysis Center of University of Tsukuba for the measurements of NMR and MALDI-TOF-MS spectra. The authors also thank Prof. K. Osakada, Prof. D. Takeuchi, Dr. Y. Tsuchido, Prof. Y. Nishihara, and Prof. H. Mori for the elemental analysis and high temperature GPC measurements. This study was supported by Grant-in-Aid for Scientific Research (17K05973, 17H03063) and Scientific Research on Innovative Areas (17H05141) from JSPS.

### Notes and references

- 1 S.-L. Suraru, J. A. Lee and C. K. Luscombe, *ACS Macro Lett.*, 2016, **5**, 724–729.
- 2 J.-R. Pouliot, F. Grenier, J. T. Blaskovits, S. Beaupré and M. Leclerc, *Chem. Rev.*, 2016, **116**, 14225–14274.
- 3 H. Bohra and M. Wang, *J. Mater. Chem. A*, 2017, **5**, 11550–11571.
- 4 M. Wakioka and F. Ozawa, *Asian J. Org. Chem.*, 2018, **7**, 1206–1216.
- 5 N. S. Gobalasingham and B. C. Thompson, *Prog. Polym. Sci.*, 2018, **83**, 135–201.
- 6 J. Kuwabara and T. Kanbara, *Bull. Chem. Soc. Jpn.*, 2019, **92**, 152–161.
- 7 J. Kuwabara, T. Yasuda, S. J. Choi, W. Lu, K. Yamazaki, S. Kagaya, L. Han and T. Kanbara, *Adv. Funct. Mater.*, 2014, **24**, 3226–3233.
- 8 J. Kuwabara, *Polym. J.*, 2018, **50**, 1099–1106.
- 9 R. Matsidik, A. Luzio, S. Hameury, H. Komber, C. R. McNeill, M. Caironi and M. Sommer, *J. Mater. Chem. C*, 2016, **4**, 10371–10380.
- 10 Q. Wang, R. Takita, Y. Kikuzaki and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 11420–11421.
- 11 W. Lu, J. Kuwabara and T. Kanbara, *Macromolecules*, 2011, **44**, 1252–1255.
- 12 R. Matsidik, H. Komber, A. Luzio, M. Caironi and M. Sommer, *J. Am. Chem. Soc.*, 2015, **137**, 6705–6711.
- 13 A. S. Dudnik, T. J. Aldrich, N. D. Eastham, R. P. H. Chang, A. Facchetti and T. J. Marks, *J. Am. Chem. Soc.*, 2016, **138**, 15699–15709.
- 14 F. Lombeck, R. Matsidik, H. Komber and M. Sommer, *Macromol. Rapid Commun.*, 2015, **36**, 231–237.
- 15 B. Liégault, D. Lapointe, L. Caron, A. Vlassova and K. Fagnou, *J. Org. Chem.*, 2009, **74**, 1826–1834.
- 16 C. A. Fleckenstein and H. Plenio, *Chem. Soc. Rev.*, 2010, **39**, 694–711.
- 17 G. C. Fortman and S. P. Nolan, *Chem. Soc. Rev.*, 2011, **40**, 5151–5169.
- 18 D. Lapointe and K. Fagnou, *Chem. Lett.*, 2010, **39**, 1118–1126.
- 19 T. Korenaga, N. Suzuki, M. Sueda and K. Shimada, *J. Organomet. Chem.*, 2015, **780**, 63–69.
- 20 M. Lafrance, D. Shore and K. Fagnou, *Org. Lett.*, 2006, **8**, 5097–5100.
- 21 H. A. Chiong and O. Daugulis, *Org. Lett.*, 2007, **9**, 1449–1451.
- 22 D. Roy, S. Mom, M. Beaupérin, H. Doucet and J.-C. Hierso, *Angew. Chem. Int. Ed.*, 2010, **49**, 6650–6654.
- 23 D. Ghosh and H. M. Lee, *Org. Lett.*, 2012, **14**, 5534–5537.
- 24 S.-C. Yin, Q. Zhou, X.-Y. Zhao and L.-X. Shao, *J. Org. Chem.*, 2015, **80**, 8916–8921.
- 25 O. Y. Yuen, M. P. Leung, C. M. So, R. W. Y. Sun and F. Y. Kwong, *J. Org. Chem.*, 2018, **83**, 9008–9017.
- 26 S. Tamba, Y. Okubo, S. Tanaka, D. Monguchi and A. Mori, *J. Org. Chem.*, 2010, **75**, 6998–7001.
- 27 M. Lesieur, F. Lazreg and C. S. J. Cazin, *Chem. Commun.*, 2014, **50**, 8927–8929.

- 28 W. Lu, J. Kuwabara, T. Iijima, H. Higashimura, H. Hayashi and T. Kanbara, *Macromolecules*, 2012, **45**, 4128–4133.
- 29 F. Lombeck, H. Komber, S. I. Gorelsky and M. Sommer, *ACS Macro Lett.*, 2014, **3**, 819–823.
- 30 J. Kuwabara, M. Sakai, Q. Zhang and T. Kanbara, *Org. Chem. Front.*, 2015, **2**, 520–525.
- 31 J. Kuwabara, Y. Fujie, K. Maruyama, T. Yasuda and T. Kanbara, *Macromolecules*, 2016, **49**, 9388–9395.
- 32 A. Faradhiyani, Q. Zhang, K. Maruyama, J. Kuwabara, T. Yasuda and T. Kanbara, *Mater. Chem. Front.*, 2018, **2**, 1306–1309.
- 33 J. A. Lee and C. K. Luscombe, *ACS Macro Lett.*, 2018, **7**, 767–771.
- 34 L. J. Kang, L. Xing and C. K. Luscombe, *Polym. Chem.*, 2019, **10**, 486–493.
- 35 S. Caddick, F. G. N. Cloke, P. B. Hitchcock, J. Leonard, A. K. de K. Lewis, D. McKerrecher and L. R. Titcomb, *Organometallics*, 2002, **21**, 4318–4319.
- 36 E. G. Gordeev, D. B. Eremin, V. M. Chernyshev and V. P. Ananikov, *Organometallics*, 2018, **37**, 787–796.
- 37 A. Ichige, H. Saito, J. Kuwabara, T. Yasuda, J.-C. Choi and T. Kanbara, *Macromolecules*, 2018, **51**, 6782–6788.
- 38 M. Hoyos, R. S. Sprick, C. Wang, M. L. Turner and O. Navarro, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 4155–4160.
- 39 S. Díez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595–7606.