

Selective Modulation of Energy Levels of Frontier Orbitals in Solid-state Luminescent Boron-fused Azomethine Polymers with Orthogonal Orientation to the Main-chains

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Abstract

The development of the polymers with film luminescence and property tuning is still a relevant topic due to concentration quenching which most of organic luminophores suffer from. Based on boron-fused azomethine (BAm) complexes which can show aggregation-induced emission (AIE) and crystallized-induced emission (CIE), we previously obtained solid-state luminescent polymers. In this report, we synthesized the π -conjugated polymers involving the orthogonally-oriented BAm to the main-chains. In particular, the synthesized polymers have quite different properties from the parallelly-oriented BAm-consisting of π -conjugated polymers which were previously reported. The synthesized polymers can show intense luminescence in solution and film. Moreover, we found that energy levels of one of frontier molecular orbitals (FMOs) can be selectively perturbed depending on the ligand structure. Furthermore, by selecting condensed reagents in the azomethine bond formation reaction, the monomer structure followed by perturbed FMO can be determined. Finally, we observed that the synthesized polymers exhibit steady emission both in solution and film in the near-infrared (NIR) region ($\lambda_{\text{PL}} = 686 \text{ nm}$, $\Phi_{\text{PL}} = 4\%$ in solution, $\lambda_{\text{PL}} = 709 \text{ nm}$, $\Phi_{\text{PL}} = 3\%$ in film). Computer calculations support these experimental data. In this study, the new series of solid-state luminescent π -conjugated polymers with tunability of energy levels is demonstrated.

Introduction

Excellent light absorptive and emissive properties, carrier transporting abilities and film formability of π -conjugated polymers have attracted attention for applying to chemical sensors,¹ organic electroluminescence devices (OLEDs),² and organic photovoltaics (OPVs)³. Although superior materials have been developed so far, the strategy to obtain bright emission from polymer films has been still strongly required because the film emission is often annihilated due to concentration quenching caused by intermolecular interaction among the polymer chains.⁴ One of the effective design strategies to avoid concentration quenching is the concept of insulated molecular wires, in which the π -conjugated polymer chain is covered and protected by bulky substituents from π - π stacking.⁵ As another instance, unlike conventional organic luminophores, AIE- and CIE-active molecules show weak or negligible emission in solution, whereas their emission properties are greatly enhanced in aggregation and crystal, respectively. We have reported that the luminophores with AIE⁶ and/or CIE⁷ properties are applicable as a monomer for constructing π -conjugated polymers with intense film luminescent properties.⁸

We have recently proposed the concept of “element-blocks” which are functional structural units containing heteroatom.⁹ By the combination of element-blocks, we can create “element-block polymers” having unique functions originating from the loaded heteroatom.⁹ We have discovered that boron-fused azobenzene (BAz)¹⁰ and BAm complexes¹¹ can work as AIE- and CIE-active element-blocks. According to mechanistic studies, it was revealed that the molecular motions triggered in the excited state originated from their potential flexible and bendable structures should be a key factor for expressing AIE and CIE behaviors.^{8b,10a,11a} Highly-efficient emission properties in both solution and

film were obtained from the polymers containing these element-blocks.¹² By incorporating these complexes into polymer main-chains, molecular motions would be effectively suppressed, followed by inhibition of emission annihilation in the solution state. Furthermore, the perpendicularly-protruded substituent at boron plays an important role in inducing film emission by inhibiting intermolecular π - π interaction.^{10e} Additionally, since BAZ and BAm complexes are used as strong and moderate acceptors, respectively, the emission color can be tuned from the yellow to NIR region by forming donor-acceptor (D-A) systems with electron-donating comonomers, such as fluorene and bithiophene, through the polymer main-chains.^{10a-e,11b,f}

Herein, we show quite different electronic properties of the π -conjugated polymers consisting of the orthogonally-orientated BAm units in the main-chain from those of the parallelly-oriented ones which were previously reported (Figure 1).^{11b} The synthesized polymers show intense emission both in solution and film. Especially, their emission wavelengths can be tuned through the selective modulation of energy levels of one of FMOs. Moreover, by selecting condensation reagents in the monomer synthesis,^{13,14} the ligand structure followed by the selectively-perturbed highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) can be determined. Finally, we obtained NIR-luminescent film materials based on our polymers. These electronic properties were well supported by quantum calculations. Hence, we can say that modulations of energy level of one of FMOs were accomplished.

Figure 1

Synthesis

Scheme 1 represents the synthetic routes for bis-brominated BAm monomers, **BAmF-Br**, **BAmPh-Br** and **prBAmPh-Br**. Formylation of the starting compound 2,5-dibromophenol (**1**) gave compound **2** in 16% isolated yield. To investigate the effect of the fused structures with a phenyl or an alkyl group, condensation reactions between **2** and 2-aminobenzyl alcohol (**3**) or 3-amino-1-propanol (**5**) were carried out. Then, the O,N,O-type tridentate ligands **4** and **6** were obtained in 57% and 68% isolated yield, respectively. The ligand **4** was converted to the BAm complexes, **BAmF-Br** and **BAmPh-Br** by the condensation reactions with boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{Et}_2\text{O}$) and dichlorophenylborane (PhBCl_2) in 85% and 82% isolated yield, respectively. The fluorine and the phenyl group at boron were introduced for evaluating the substituent effect of the vertically-protruded moiety mainly on solid-state luminescent properties. The ligand **6** was used for preparing **prBAmPh-Br**, and the condensation reaction with phenyl boronic acid ($\text{PhB}(\text{OH})_2$) provided the target compound in 36% isolated yield.

Next, the polymerization with the Migita–Kosugi–Stille cross coupling¹⁵ was conducted with BAm monomers and fluorine (**FL**) or bithiophene (**BT**) comonomer with the catalyst $\text{Pd}_2(\text{dba})_3$ (dba = dibenzylideneacetone) using 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) as a phosphine ligand. The reaction can be executed under a neutralized condition which is significant to avoid undesired decomposition of the boron complexes. After reactions, alternating copolymers **P-BAmF-FL**, **P-BAmF-BT**, **P-BAmPh-BT**, and **P-prBAmPh-BT** were obtained (Scheme 2). These polymers were purified and collected as a solid by reprecipitation into a huge amount of methanol from the chloroform solution to remove small molecular-weight products and catalysts.

The molecular weights of the obtained polymers were determined by gel permeation chromatography (GPC) with polystyrene standards (Table 1). Preservation of the boron complex moieties in the polymer chains was confirmed from detection of the repeating units with matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOFMS). We were not able to obtain the other FL polymers with sufficient molecular weights because the reactivity between BAm and FL monomers was relatively low compared to that between BAm and BT ones. In addition, **BAmF**, **BAmPh**, and **prBAmPh**, were synthesized following Scheme 3 to investigate properties of the monomeric units. **BAmF** and the tridentate ligand **7** were prepared according to the previous literature.^{11b} All the synthesized compounds had good solubility in common organic solvents such as toluene, chloroform, dichloromethane and tetrahydrofuran, and can be characterized by ¹H, ¹³C and ¹¹B NMR spectroscopy and MS spectrometry (see the Supporting Information, SI). From the characterization data, we concluded that the samples have the designed structures and enough purity for further analyses.

Schemes 1, 2 and 3, Table 1

Results and discussion

Optical measurements

Optical properties of the synthesized monomeric units and polymers were examined in the toluene-abundant mixed solvent (1.0×10^{-5} M in toluene/CHCl₃ = 99/1 v/v, per repeating unit for polymers). The spectroscopic data are summarized in Figures 2 and 3, Tables 2 and 3. In UV-vis absorption spectra of **BAmF**, **BAmPh** and **prBAmPh**, there

were two strong absorption bands around 300 and 400 nm, which were originating from π - π^* transition in the BAm unit (Figure 2A). The bathochromic shifts of the absorption bands were clearly observed in the polymers (Figure 2B). This means that the π -conjugated systems should be effectively expanded through the polymer main-chains. The longest absorption band of **P-BAmPh-BT** was located in the longer wavelength region than that of **P-BAmPh-FL**. The BT units with alkyl chains at 3,3' positions induce twisted structures due to their steric hindrance. However, because the BT units generally work as the stronger electron-donor than the FL units, stronger D-A interaction should be formed in the BT-containing polymers.^{11b} **P-BAmF-BT** and **P-BAmPh-BT** exhibited similar absorption spectra. Although we previously reported that the electron-accepting ability of the fluorine at boron was stronger than that of the phenyl group,^{10e} the difference was hardly observed from the comparison with **P-BAmF-BT** and **P-BAmPh-BT**. It is likely that the perpendicular substituents can form slight interaction with polymer main-chains in solution. **P-BAmPh-BT** had better solubility in common organic solvents than **P-BAmF-BT**. It is probably because the steric effect of the phenyl group could contribute to improving solubility of the polymers. **P-prBAmF-BT** had shorter absorption wavelengths than the other BT polymers. Weaker electron-accepting ability of **prBAmF** than those of **BAmF** and **BAmPh** might be proposed. The phenyl group should increase the electron-accepting ability of the BAm complexes because of π -electron delocalization up to the outer phenyl moiety. All polymers had good film formability, and we prepared thin films from chloroform solutions by a spin-coating method on a quartz substrate. Consequently, the spectral shapes both in solution and film were almost similar although slight bathochromic shifts of the spectra were observed in film (Table 3, Figure 2C). These data imply that the formation of ordered structures as well as tight chain assembly could

be disturbed in the condensed state through the steric protection with the perpendicularly-protruded substituent at boron.

Next, we investigated photoluminescence (PL) properties of the monomeric units and polymers under the same condition as the UV-vis absorption spectrum measurements (Table 2, Figure 3). The monomeric units showed weak emission (absolute PL quantum yield, $\Phi_{\text{PL}} < 1\%$) in solution (Figure 3A). In contrast, the emission intensity was largely enhanced in solid of **BAmF** and **BAmPh** (Figure 3B). These are typical AIE and CIE behaviors. The solid-state emission in AIE and CIE properties is a common feature of the BAm complexes. The fast non-radiative deactivation can be promoted in solution by structural relaxation with bending motion after photoexcitation, whereas these molecular motions should be restricted in solid.^{10f,11a} In contrast, such an emission enhancement was not observed in **prBAmPh**. Because the π -conjugated system of **prBAmPh** is smaller than those of the others, it is assumed that emission ability might be intrinsically lower. Otherwise, molecular motions might not be restricted by intermolecular interactions even in the solid state. On the other hand, intense emission was observed from all polymers even in a diluted solution (Figure 3C). This is because the expanded π -conjugated systems reinforce rigidity of polymer chains and subsequently restrict the molecular motions, which induce emission annihilation, at the BAm complexes.^{11b} The PL peak-top wavelengths were varied by the combination of the monomers, similarly to absorption data. In solution, **P-BAmF-FL** and **P-BAmF-BT** showed yellow ($\lambda_{\text{PL}} = 568$ nm) and deep-red ($\lambda_{\text{PL}} = 694$ nm) emissions, respectively. Because of the stronger electron-donating ability of BT units than that of FL ones, a narrower energy gap should be realized, followed by emission with the peaks in the longer wavelength region. Interestingly, the emission wavelengths were much more bathochromic-shifted than those of parallelly-

oriented P-BAmF-FL (**P_P-FL**) ($\lambda_{\text{PL}} = 538 \text{ nm}$) and P-BAmF-BT (**P_P-BT**) ($\lambda_{\text{PL}} = 613 \text{ nm}$) that we previously reported (Figure S1 and Table S1).^{11b} The deep-red emission ($\lambda_{\text{PL}} = 686 \text{ nm}$) was exhibited from **P-BAmPh-BT** and the substituent effect at boron on electronic states of the polymers was hardly observed in the excited state. **P-prBAm-BT** had the intense orange emission ($\lambda_{\text{PL}} = 633 \text{ nm}$, $\Phi_{\text{PL}} = 15\%$) owing to sufficient extension of π -conjugation through the polymer main-chains and construction of the D–A system although the monomeric unit showed very weak emission ($\Phi_{\text{PL}} < 1\%$) regardless of the condition.

As we expected, the emission efficiency of the polymers was preserved in film by avoiding concentration quenching (Table 3, Figure 3D). It can be said that the solid-state emissive property of the BAm complexes is inherited by the polymers. It should be noted that **prBAmPh** also has a potential to exhibit solid-state emission because **P-prBAm-BT** retained intense emission in film. The slightly bathochromic shift was observed in the emission spectrum with the film. In particular, we observed NIR emission from **P-BAmPh-BT** ($\lambda_{\text{PL}} = 709 \text{ nm}$, $\Phi_{\text{PL}} = 3\%$). The development of the intense NIR emission from π -conjugated polymer films are still needed. These data mean that our materials might be able to meet a demand of polymer films with efficient NIR-luminescent properties.¹⁶

To obtain more insight into the emission properties, we measured PL lifetimes and calculated a radiative constant (k_{r}) and a non-radiative constant (k_{nr}) (Figure S2, Tables 2 and 3). The values of k_{r} in monomeric units were quite small ($k_{\text{r}} \sim 10^6 \text{ s}^{-1}$) probably due to the small π -conjugation and structural deformation of the BAm complexes in the excited state. In contrast, the values were largely enhanced in solid ($k_{\text{r}} > 10^7 \text{ s}^{-1}$).^{11a} This might be because of the electronic intermolecular interaction of the luminophores and the

prohibition of the structural deformation. The increase in the values of k_r was also observed from the polymers. The k_r values were detected in the moderate range ($k_r \sim 10^7 \text{ s}^{-1}$) from **P-BAmF-FL**, **P-BAmF-BT**, and **P-BAmPh-BT**, whereas the significant large value was observed from **P-prBAmPh-BT** ($k_r \sim 10^8 \text{ s}^{-1}$). This indicates that main-chain π -conjugation is effectively expanded through **P-prBAmPh-BT**. Increase in the k_{nr} values with the emission band in the long wavelength region might be explained by the energy gap law¹⁷ and the flexibility of monomeric units. Surprisingly, the values of k_r and k_{nr} were almost same between in solution and in film. This means that the optical properties are highly preserved regardless of molecular environments. These results suggest that inherent solid-state emissive properties of the BAm complexes are suitable for preparing the energy-tunable luminescent π -conjugated polymers.

Figures 2,3 and Tables 2,3

Cyclic voltammetry

To estimate energy levels of molecular orbitals (MOs) of the BAm derivatives, we carried out a cyclic voltammetry (CV) measurement. The results are summarized in Figure S3 and Table 4. The LUMO energy levels were calculated from the onset of the reduction curve,¹⁸ and then HOMO energy levels were estimated with optical energy gaps ($E_{g,opt}$) obtained from the long-wavelength edge in the UV–vis absorption spectra (Figure 2). In the monomeric units, the HOMO and LUMO energy levels of **BAmF** and **BAmPh** were lower than those of **prBAmPh**, indicating that the fused phenyl ring contributes to reduction of energy levels of MOs. Moreover, the phenyl group at boron especially elevated energy levels of HOMOs. Large increases in HOMO energy levels were detected

in all polymers, and slight decreases in LUMO ones were observed in BT polymers. These results imply that FL and BT units work as an electron-donor and especially the BT polymers involve the strong D–A interaction through the polymer main-chain.

Table 4

2.4 Theoretical calculation

To support experimental results, we conducted theoretical calculations with density functional theory (DFT) and time dependent DFT (TD-DFT) at B3LYP/6-311G(d,p) level. The calculation details are described in SI. The model compounds with the methyl-substituted bithiophene units connected at both sides of the monomeric units are used to save the calculation cost with the polymers (Figure S4). Both in the monomeric units and polymers, variation tendency of calculated HOMO and LUMO energy levels (Figure 4A) and $S_0 \rightarrow S_1$ transition energies (Figure 4B) were precisely matched to the experimental results. This means that this calculation method is suitable for theoretically investigating detailed properties of monomeric units and polymers.

In the monomeric units, HOMO and LUMO were delocalized throughout the structures (Figure S5). The large elevation of HOMO energy levels of **BAmPh** and **prBAmPh** should be attributable to orbital contribution of the phenyl group at boron. In contrast, the orbital distribution was altered by extension of the π -conjugation (Figures 5 and S5). In the polymers, HOMO was delocalized through the main-chain and the azomethine moiety did not contribute it. Meanwhile, LUMO was mainly localized at the BAm unit including the azomethine moiety. Consequently, it should be emphasized that the asymmetric orbital distribution provided selective elevation of HOMO energy level

in the orthogonally-oriented M-BAmF-BT (**O_M-BT**) compared to parallelly-oriented M-BAmF-BT (**P_M-BT**) where the HOMO energy level was stabilized by the azomethine moiety (Figure 5A). The similar tendency was also observed from M-BAmF-FT derivatives (**O_M-FT** and **P_M-FT**) (Figure S6). On the other hand, interestingly, the selective increase in the LUMO energy level was observed in **M-prBAmPh-BT** (Figure 5B) compared to in **M-BAmPh-BT**. In **M-BAmPh-BT**, there was little contribution of the azomethine moiety to HOMO, meanwhile LUMO was expanded to the outer phenyl group of the BAm unit. The contribution of the phenyl group should be responsible for lowering the LUMO energy level of **M-BAmPh-BT**. As a result, in the absence of the phenyl group, the selective elevation of LUMO energy levels was induced. We also estimated the same evaluation with the model compounds having three repeating units, and the similar tendency was observed (Figure S7). From these data, we can say that selective modulation of one of energy levels of FMOs is available in the orthogonally-oriented BAm polymers. In addition, since the introduction of the benzene ring can be programmed at the synthetic step by selecting the condensed reagents, desired optical properties, such as NIR emission, might be able to be obtained according to the preprogrammed design.

Figures 4 and 5

Stability tests

Finally, we conducted thermal stability and photostability tests of the obtained compounds to show potentials of the polymers for material applications. From evaluation of thermal decomposition temperatures (T_d s) with thermogravimetric analysis (TGA), the polymers highly increased thermal stability by from 130 to 170 °C compared to the monomeric units (Figure S8 and Table S2). It is noted that the polymers containing phenyl moieties at boron have the first T_d with the similar T_d s of the corresponding monomers. Decomposition of the boron complexes should occur at this step. Photostability tests were carried out by irradiation of UV light with a transilluminator (365 nm, 6,500 $\mu\text{W cm}^{-2}$) in a diluted solution (1.0×10^{-5} M in toluene, per repeating unit for polymers), and the decomposition rates were estimated from the reduction of the peak-top absorbance in the longest wavelength region in UV-vis absorption spectra. The results are summarized in Figure S9. The monomers were almost completely decomposed within 20 min under the UV irradiation. We previously reported the non-emissive boron complex exhibited photodegradation through elimination of boron.^{10a} In contrast, the polymers largely enhanced the photostability with preservation of the original spectra by from 72 to 97% even after 60 min irradiation of the UV light. From these experiments, it can be said that polymerization has a potential to provide enough stability to functional monomers to use various material applications.

Conclusion

We synthesized BAm complexes and investigated their optical properties. The monomeric units had an AIE property. Moreover, expansion of the π -conjugation clearly enhanced the emission performances. The BAm copolymers exhibited intense emission

both in solution and film. Significantly, we demonstrate that one of energy levels of FMOs can be selectively modulated in the orthogonally-oriented BAm polymers whether the benzene ring was fused or not. Their electronic properties were predictable by theoretical calculation. Furthermore, intense film emission was observed in the NIR region, which is originated from the narrow energy gap. Additionally, the obtained polymers had high thermal and photostability. Thus, it can be shown that they have favorable properties for solid-state luminescent materials, such as polymer-based OLEDs and chemical sensors. In this study, we show variation of molecular designs to create luminescent π -conjugated polymer films with unique functions by changing the connection motif of the monomeric unit.

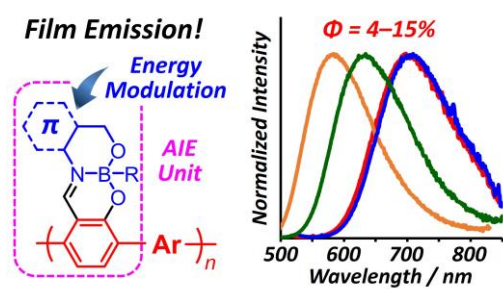
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TOC



We demonstrate energy levels of the π -conjugated polymers for the luminescent film can be controlled by selecting the fused structure.

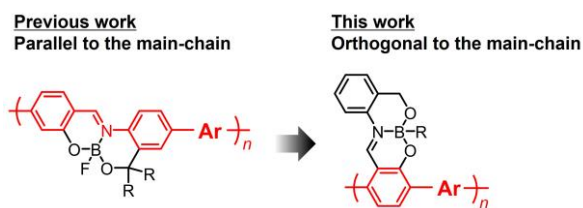
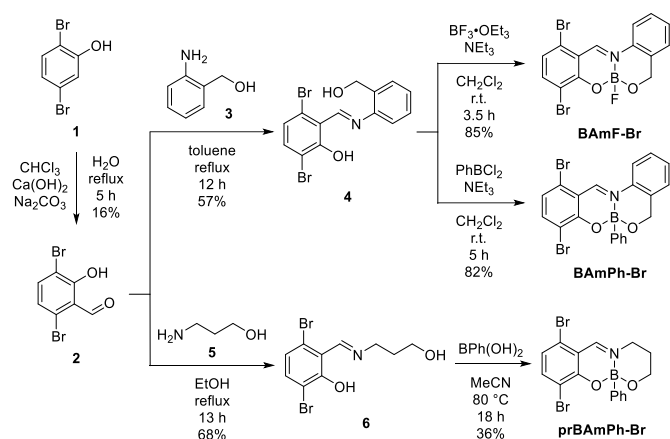
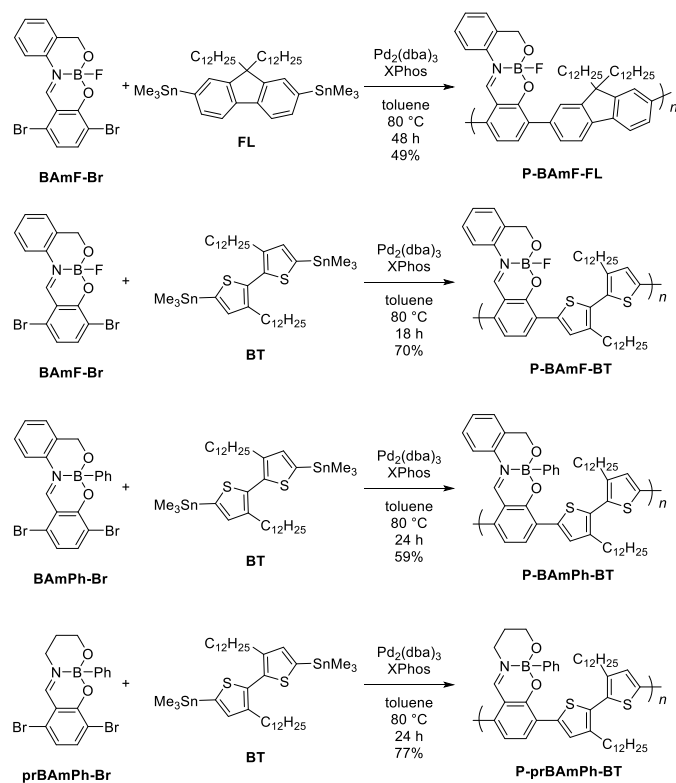


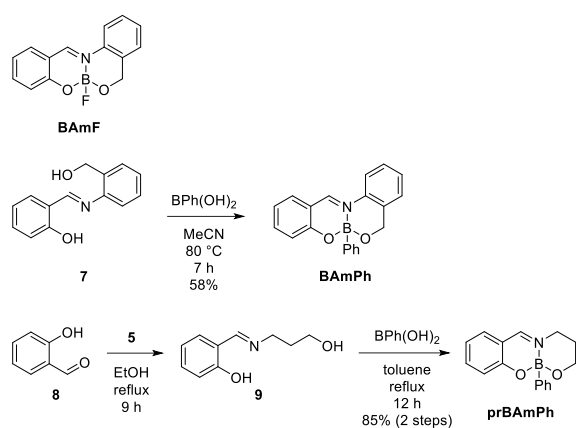
Figure 1. Concept of BAM-based π -conjugated polymers with different connection positions.



Scheme 1. Syntheses of monomers, **BAmF-Br**, **BAmPh-Br** and **prBAmPh-Br**.



Scheme 2. Synthesis of polymers, **P-BAmF-FL**, **P-BAmF-BT**, **P-BAmPh-BT** and **P-prBAmPh-Br**.



Scheme 3. Syntheses of monomeric units, **BAmPh**, **prBAmPh**, and structure of **BAmF**.

Table 1. Molecular weights and isolated yields of the synthesized polymers

	M_n^a /kDa	M_w^a /kDa	M_w/M_n	n	yield /%
P-BAmF-FL	10.3	15.7	1.5	14	49
P-BAmF-BT	20.8	39.1	1.9	28	70
P-BAmPh-BT	16.9	29.8	1.8	21	59
P-prBAmPh-BT	7.9	22.4	2.8	10	77

^a Determined by gel permeation chromatography (GPC) with polystyrene standards

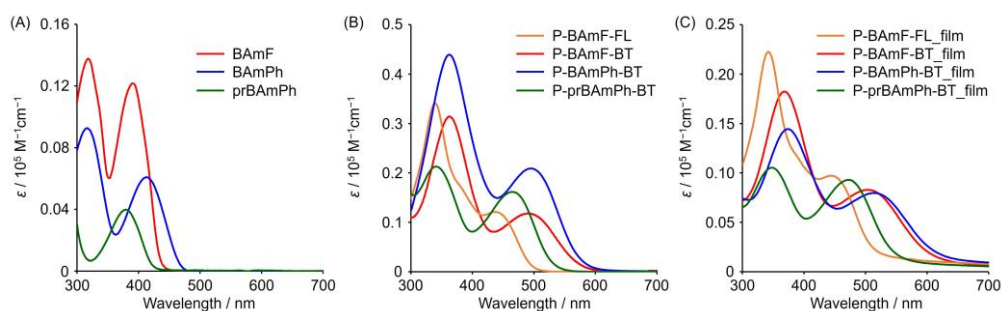


Figure 2. UV-vis absorption spectra of (A) BAm monomeric units, (B) polymers in toluene/ CHCl_3 = 99/1 v/v (1.0×10^{-5} M for monomeric units, 1.0×10^{-5} M per repeating unit for polymers) and (C) in film.

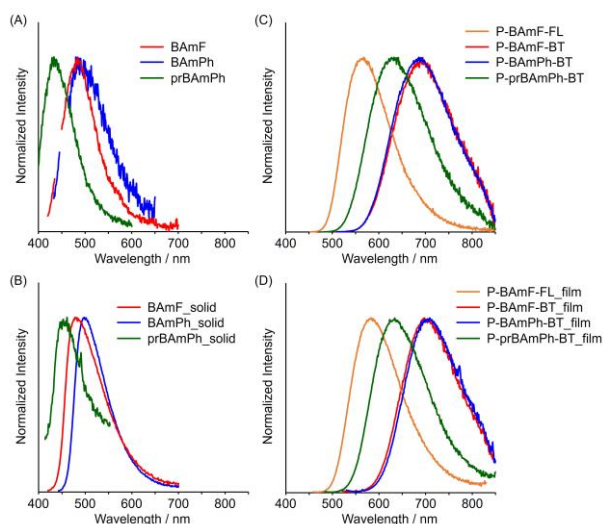


Figure 3. PL spectra of BAm (A) monomeric units and (B) polymers in toluene/ CHCl_3 = 99/1 v/v (1.0×10^{-5} M for monomeric units, 1.0×10^{-5} M per repeating unit for polymers). PL spectra of BAm (C) monomeric units in solid and (D) polymers in film, excited at wavelengths of absorption maxima.

Table 2. Optical data of the BAm monomeric units and polymers in solution

	λ_{abs}^a /nm	ϵ_{abs}^a /M ⁻¹ cm ⁻¹	λ_{PL}^a /nm	$\Phi_{\text{PL}}^{a,b}$ /%	$\tau_{\text{av}}^{a,c}$ /ns	k_{r}^d /10 ⁸ s ⁻¹	k_{nr}^d /10 ⁸ s ⁻¹
BAmF	391	12000	486	0.5	3.5	0.015	2.9
BAmPh	413	6100	491	0.3	0.37	0.080	27
prBAmPh	380	4000	437	0.3	1.5	0.020	6.8
P-BAmF-FL	340, 437	34000, 12000	568	18	2.4	0.77	3.4
P-BAmF-BT	363, 491	31000, 12000	694	4	0.82	0.50	12
P-BAmPh-	362,	44000,	686	4	0.69	0.55	14
BT	495	21000					
P-prBAmPh-	340,	21000,	633	18	1.3	1.4	6.2
BT	465	16000					

^a In toluene/CHCl₃ = 99/1 v/v (1.0×10⁻⁵ M for monomeric units, 1.0×10⁻⁵ M for monomeric units and 1.0×10⁻⁵ M per repeating unit for polymers), excited at wavelengths of absorption maxima for PL.

^b Absolute PL quantum yield excited at wavelengths of absorption maxima.

^c Average of emission lifetime at λ_{PL} .

^d $k_{\text{r}} = \Phi_{\text{PL}}/\tau_{\text{av}}$, $k_{\text{nr}} = (1 - \Phi_{\text{PL}})/\tau_{\text{av}}$

Table 3. Optical data of the BAm monomeric units in solid and polymers in film

	λ_{abs}^a /nm	λ_{PL}^a /nm	$\Phi_{\text{PL}}^{a,b}$ /%	$\tau_{\text{av}}^{a,c}$ /ns	k_{r}^d /10 ⁸ s ⁻¹	k_{nr}^d /10 ⁸ s ⁻¹
BAmF	— ^e	482	8	2.2	0.35	4.1
BAmPh	— ^e	498	10	0.71	1.4	1.3
prBAmPh	— ^e	453	0.2	0.72	0.028	14
P-BAmF-FL	342, 444	583	15	2.9	0.53	3.0
P-BAmF-BT	368, 504	697	4	0.80	0.52	12
P-BAmPh-BT	374, 513	709	3	0.61	0.56	16
P-prBAmPh-BT	348, 472	634	15	1.2	1.2	7.0

^a Solid state for monomeric units; excited at λ_{abs} in solution for PL, and spin-coated film on the quartz substrate (0.9 cm×5 cm) prepared from chloroform solution (0.10 mL, 1000 rpm, concentration: 1.0 mg/0.30 mL) for polymers, excited at wavelengths of absorption maxima for PL.

^b Absolute PL quantum yield excited at wavelengths of absorption maxima.

^c Average of emission lifetime at λ_{PL} .

^d $k_{\text{r}} = \Phi_{\text{PL}}/\tau_{\text{av}}$, $k_{\text{nr}} = (1 - \Phi_{\text{PL}})/\tau_{\text{av}}$

^e Not measured.

Table 4. Energy levels of molecular orbitals of BAm monomeric units and polymers

	$\lambda_{\text{abs,edge}}^a / \text{nm}$	$E_{\text{g,opt}}^b / \text{eV}$	$E_{\text{onset}}^{\text{red } c} / \text{V}$	$E_{\text{LUMO}}^d / \text{eV}$	$E_{\text{HOMO}}^d / \text{eV}$
BAmF	434	2.86	−1.67	−3.13	−5.99
BAmPh	467	2.66	−1.77	−3.03	−5.69
prBAmPh	423	2.93	−2.16	−2.64	−5.57
P-BAmF-FL	496	2.50	−1.71	−3.09	−5.59
P-BAmF-BT	575	2.16	−1.56	−3.24	−5.40
P-BAmPh-BT	575	2.16	−1.66	−3.14	−5.30
P-prBAmPh-BT	529	2.34	−1.98	−2.82	−5.16

^a In toluene/CHCl₃ = 99/1 v/v (1.0×10^{−5} M for monomeric units, 1.0×10^{−5} M per repeating unit for polymers), estimated from Figure 2.

^b $E_{\text{g,opt}} = 1240/\lambda_{\text{abs,edge}}$.

^c In dichloromethane (1.0×10^{−3} M for monomeric units, 1.0×10^{−3} M per repeating unit for polymers) containing *n*Bu₄NPF₆ (0.10 M) at room temperature with a scan rate of 0.1 V s^{−1}.

^d $E_{\text{LUMO}} = -(4.8 - E_{\text{onset}}^{\text{red}})$, $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g,opt}}$.

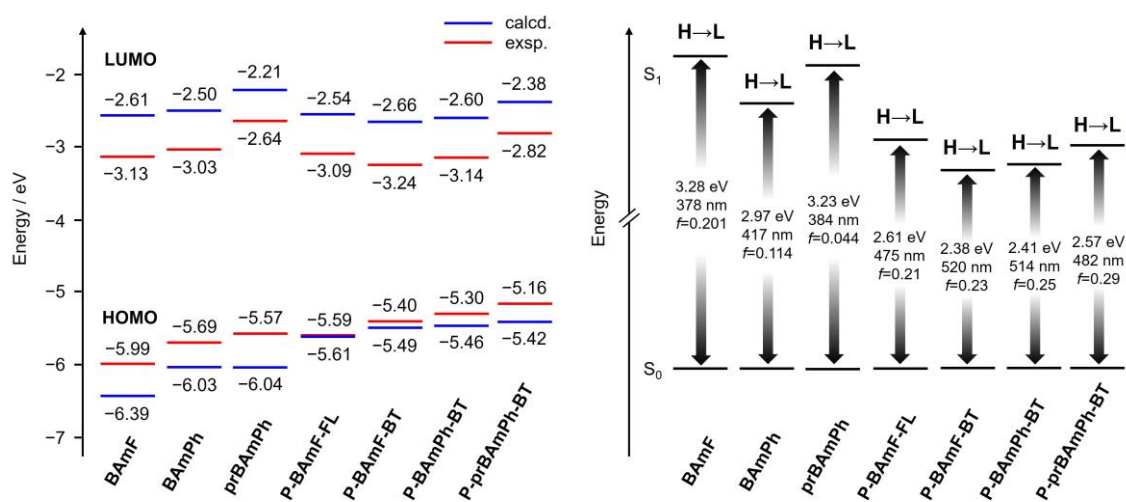


Figure 4. (A) Energy diagrams of BAM monomeric units and polymers (blue line: from DFT calculation, red line: from CV and UV-vis absorption spectra, Table 3). (B) Calculated S₀ (ground state) to S₁ (the first excited state) transition energy of BAM monomeric units and polymers assigned to HOMO (H) to LUMO (L) transition. Calculated data of polymers are obtained from model compounds.

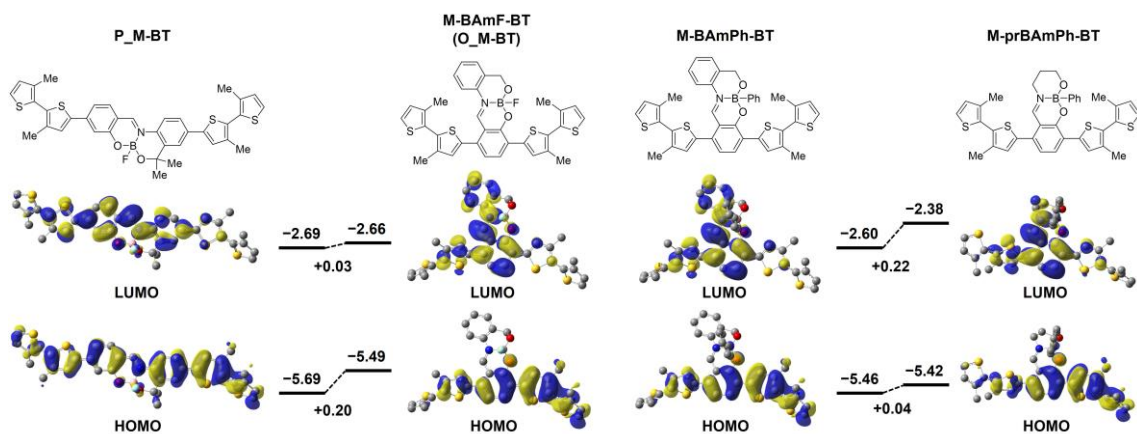


Figure 5. Chemical structures, energy diagrams, and Kohn-Sham orbitals of model compounds of polymers with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

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Supplementary Information

**Selective Modulation of Energy Levels of Frontier Orbitals in
Solid-state Luminescent Boron-fused Azomethine Polymers with
Orthogonal Orientation to the Main-chains**

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General

^1H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM AL400 spectrometer. Samples were analyzed in CDCl_3 and CD_2Cl_2 . The chemical shift values were expressed relative to tetramethylsilane (TMS) for ^1H NMR in CDCl_3 . For ^1H NMR in CD_2Cl_2 , internal standards were used. $\text{BF}_3\cdot\text{OEt}_2$ was used as a capillary standard for ^{11}B NMR. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel[®] C-300 silica gel. UV–vis–NIR absorption spectra were recorded on a SHIMADZU UV-3600i plus spectrophotometer. Photoluminescence (PL) spectra were measured on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. Absolute PL quantum efficiency was measured on a HAMAMATSU Quantaaurus-QY Plus. The PL lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using UV diode lasers (NanoLED 375 nm), and a Horiba DeltaFlex spectrofluorometer system; excitation was carried out using UV diode lasers (DeltaDiode 375 nm). Cyclic voltammetry (CV) was carried out on a BASALS-Electrochemical-Analyzer Model 600D with a grassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc^+) external reference at a scan rate of 0.1 V s^{-1} . High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a JEOL JMS-MS700 spectrometer for electron ionization (EI), a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI), a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI) and a Bruker Daltonics ultrafleXtreme for matrix assisted laser desorption ionization (MALDI). Gel permeation chromatography (GPC) was carried out on a TOSOH G3000HXL system equipped with three consecutive polystyrene gel columns (TOSOH gels: α -4000, α -3000, α -2500) using chloroform as an eluent after calibration with standard polystyrene samples. TGA was performed on an EXSTAR STA7200RV, a Hitachi High-Tech Science Corporation., with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ up to $550\text{ }^\circ\text{C}$ under nitrogen flowing ($200\text{ mL}/\text{min}$). Photostability test was carried out by UVP Benchtop UV Transilluminator, LMS-20(3UV), 254/302/365nm, 100V, 8W.

Materials

Commercially available compounds used without purification:

2,5-Dibromophenol (**1**) (BLD Pharmatech, Inc.)

Ca(OH)₂ (FUJIFILM Wako Pure Chemical Corporation)

Na₂CO₃ (FUJIFILM Wako Pure Chemical Corporation)

MgSO₄ (FUJIFILM Wako Pure Chemical Corporation)

1 M HCl for Volumetric Analysis (FUJIFILM Wako Pure Chemical Corporation)

2-Aminobenzyl alcohol (**3**) (Tokyo Chemical Industry Co, Ltd.)

Boron trifluoride diethyl etherate (≥46% BF₃ basis) (BF₃·Et₂O) (Sigma-Aldrich Co. LLC.)

Pd₂(dba)₂ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.)

2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (Strem Chemicals, Inc.)

Dichlorophenylborane (FUJIFILM Wako Pure Chemical Corporation)

Salicylaldehyde (Tokyo Chemical Industry Co, Ltd.)

3-Amino-1-propanol (**5**) (Tokyo Chemical Industry Co, Ltd.)

Phenylboronic acid (FUJIFILM Wako Pure Chemical Corporation)

Commercially available solvents:

EtOH (FUJIFILM Wako Pure Chemical Corporation), CHCl₃ (FUJIFILM Wako Pure Chemical Corporation), hexane (FUJIFILM Wako Pure Chemical Corporation), EtOAc (FUJIFILM Wako Pure Chemical Corporation), CHCl₃ (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation), toluene (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation), MeCN (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation), Et₂O (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) used without further purification. Et₃N (Kanto Chemical Co., Inc.) purified by passage through solvent purification columns under N₂ pressure.

Compounds prepared as described in the literatures

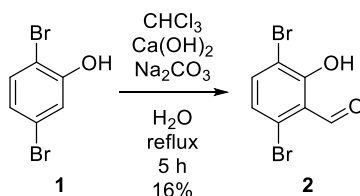
5,5'-Bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene^{1,2}

(9,9-Didodecyl-9*H*-fluorene-2,7-diyl)bis(trimethylstannane)³

BAmF⁴

Synthetic Procedures and Characterization

Synthesis of **2** (3,6-dibromo-2-hydroxybenzaldehyde)



To an aqueous mixture of Ca(OH)₂ (6.49 g, 87.6 mmol), Na₂CO₃ (22.8 g, 215 mmol) and 2,5-dibromophenol (**1**) (5.04 g, 20.0 mmol), CHCl₃ (25 mL, 63 mmol) was added dropwise under N₂ atmosphere. The mixture was refluxed for 5 h. After cooling to room temperature, the mixture was acidified with 1 M HCl aqueous solution. Then, the product was extracted with CHCl₃. Organic layer was washed with brine, dried over MgSO₄ and evaporated to afford a yellow solid. The solid was purified by chromatography on silica gel with hexane/CHCl₃ (v/v = 4/1). In recrystallization procedure (good solvent: CHCl₃, poor solvent: hexane), the target compound **2** was collected as a filtrate. After the filtrate was evaporated, further purification was carried out by recrystallization with hexane to afford **2** (0.89 g, 3.2 mmol, 16%) as a yellow solid.

R_f = 0.40 (hexane/CHCl₃ = 4/1 v/v). ¹H NMR (CDCl₃, 400 MHz) δ 12.64 (s, 1H), 10.28 (s, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz), δ 197.5, 160.4, 140.3, 126.5, 125.1, 118.2, 111.1 ppm. HRMS (APCI) calcd. for C₇H₃Br₂O₂ [M-H]⁻, 276.8505; found: 276.8506.

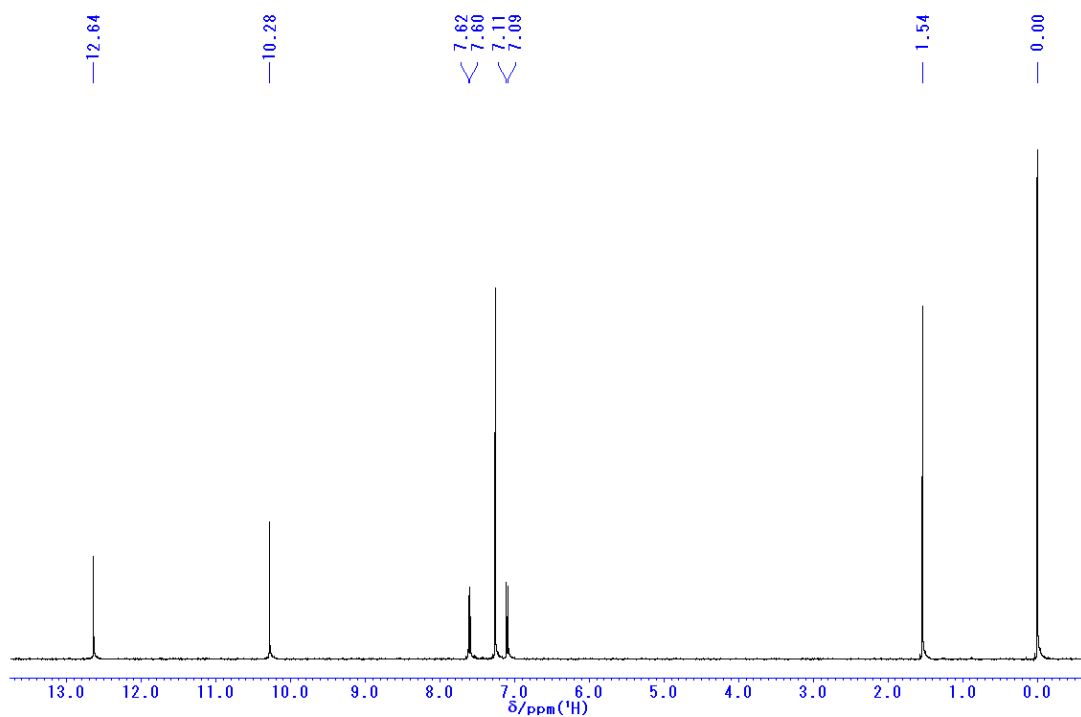


Chart S1. ^1H NMR spectrum of **2**, CDCl_3 , 400 MHz.

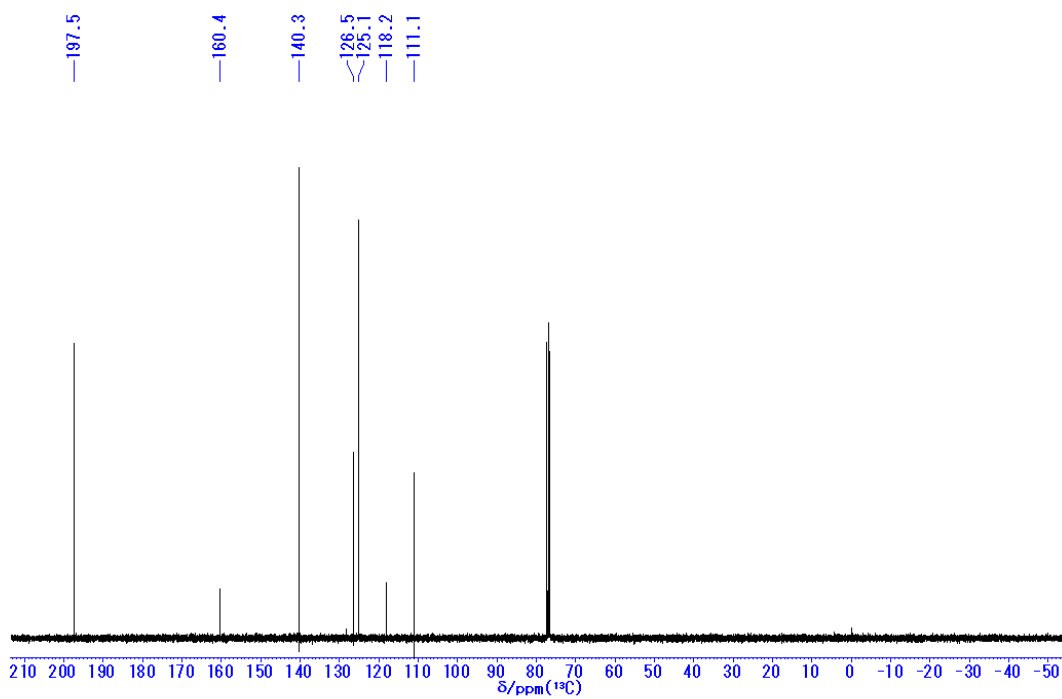
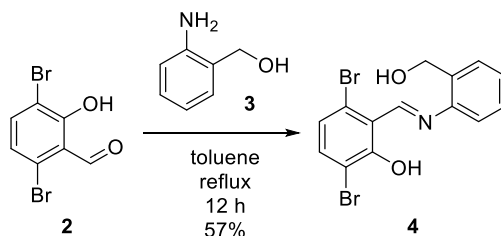


Chart S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2**, CDCl_3 , 100 MHz.

Synthesis of **4** ((*E*)-3,6-dibromo-2-(((2-(hydroxymethyl)phenyl)imino)methyl)phenol)



2 (0.14 g, 0.498 mmol) and 2-aminobenzyl alcohol (**3**) (0.06 g, 0.498 mmol) were dissolved in toluene (6 mL) under N₂ atmosphere and refluxed for 12 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel with hexane/EtOAc (v/v = 4/1) to afford **4** (0.11 g, 0.29 mmol, 57%) as an orange powder.

R_f = 0.30 (hexane/EtOAc = 4/1 v/v). ¹H NMR (CD₂Cl₂, 400 MHz) δ 9.10 (s, 1H), 7.55–7.54 (m, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.44 (dt, J = 7.6, 1.7 Hz, 1H), 7.38 (dt, J = 7.5, 1.5 Hz, 1H), 7.30 (dd, J = 7.8, 1.4 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 4.87 (s, 2H) ppm. Two exchangeable proton peaks at hydroxyl groups were not detected. ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz) δ 162.6, 161.2, 145.0, 137.4, 135.3, 129.4, 129.0, 128.4, 125.8, 124.0, 118.7, 118.1, 111.8, 62.2 ppm. HRMS (ESI) C₁₄H₁₂Br₂NO₂ calcd. for [M+H]⁺: 383.9229; found: 383.9238.

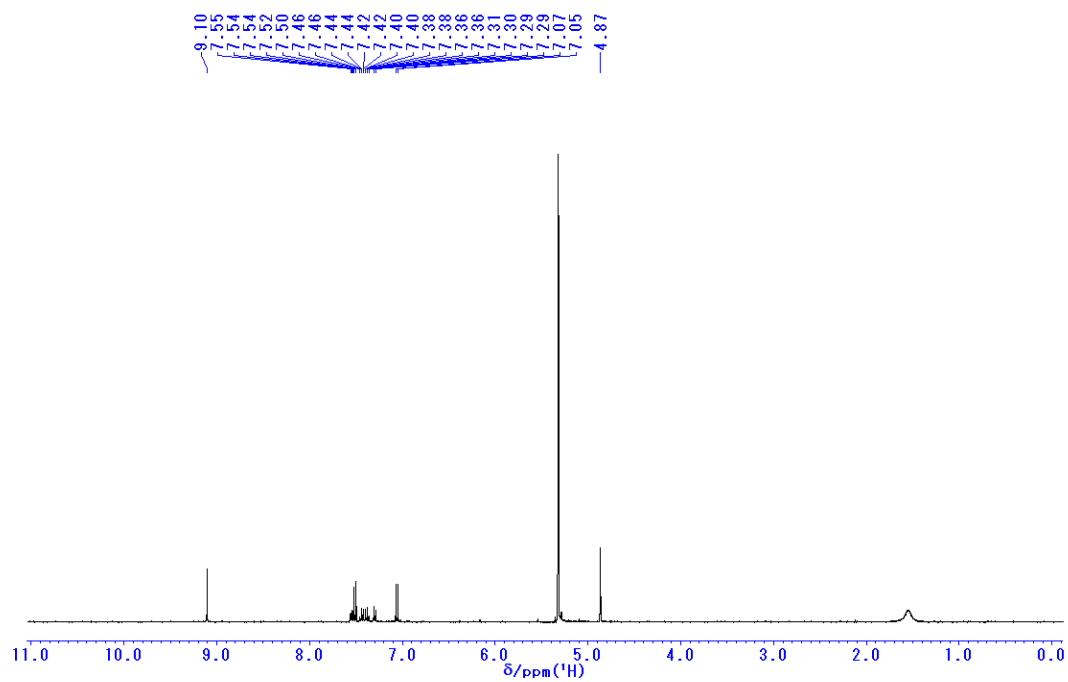


Chart S3. ^1H NMR spectrum of **4**, CD_2Cl_2 , 400 MHz.

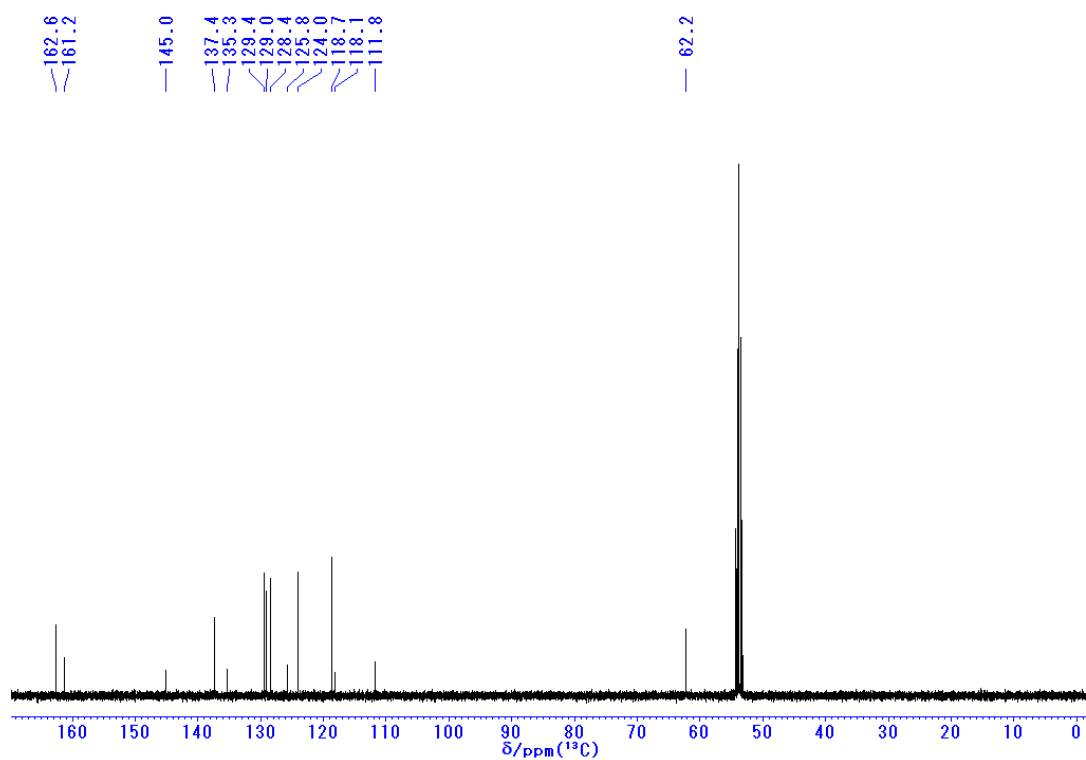
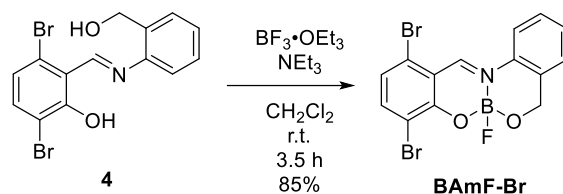


Chart S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4**, CD_2Cl_2 , 100 MHz.

Synthesis of BAmF-Br



4 (0.20 g, 0.51 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under N_2 atmosphere and triethylamine (0.7 mL, 5 mmol) was then added to the reaction mixture at room temperature. $\text{BF}_3 \cdot \text{OEt}_2$ (0.6 mL, 5 mmol) was added and stirred for 3.5 h at room temperature. The reaction mixture was quenched by H_2O . Then, the product was extracted with CH_2Cl_2 . Organic layer was washed with brine, dried over MgSO_4 and evaporated to afford **BAmF-Br** (0.18 g, 0.44 mmol, 85%) as a yellow powder.

^1H NMR (CD_2Cl_2 , 400 MHz) δ 9.14 (s, 1H), 7.75–7.71 (m, 2H), 7.49–7.45 (m, 2H), 7.28–7.26 (m, 1H), 7.17 (d, $J = 8.3$ Hz, 1H), 5.22 (d, $J = 15.6$ Hz, 1H), 5.02 (d, $J = 15.9$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) δ 158.0, 153.9, 141.1, 136.2, 135.2, 130.5, 128.6, 127.2, 125.5, 125.5, 117.8, 117.3, 113.4, 63.6 (d, $J = 3.29$ Hz) ppm. ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 1.31 (d, $J = 35.8$ Hz) ppm. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_9\text{BBr}_2\text{FNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$, 433.8969; found: 433.8970.

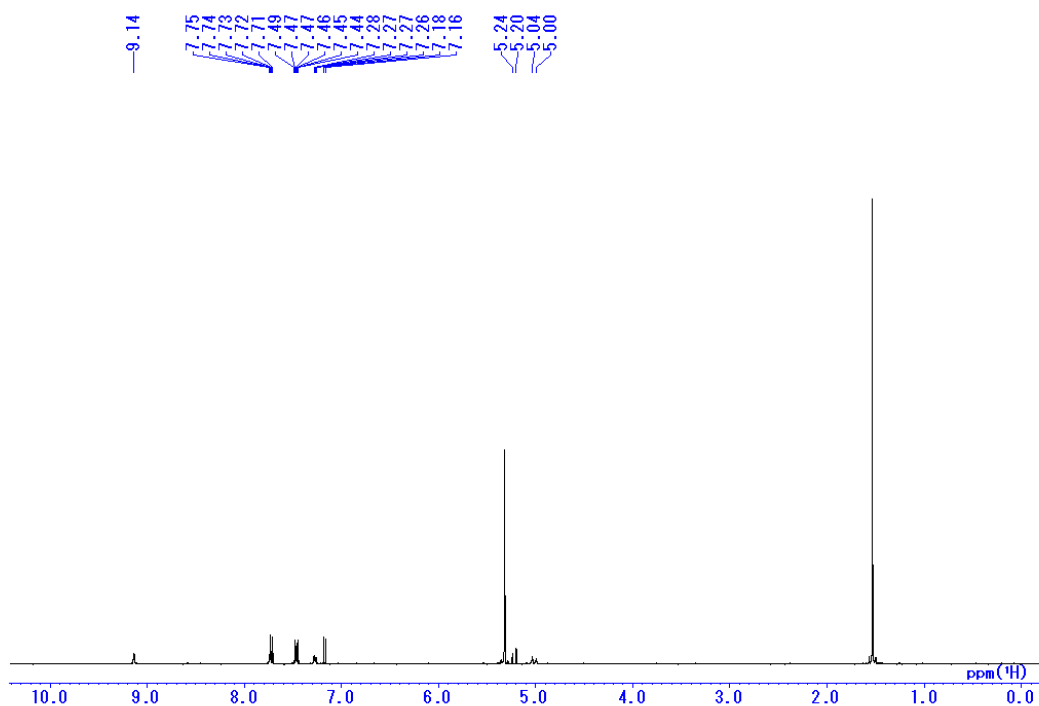


Chart S5. ^1H NMR spectrum of **BAmF-Br**, CD_2Cl_2 , 400 MHz.

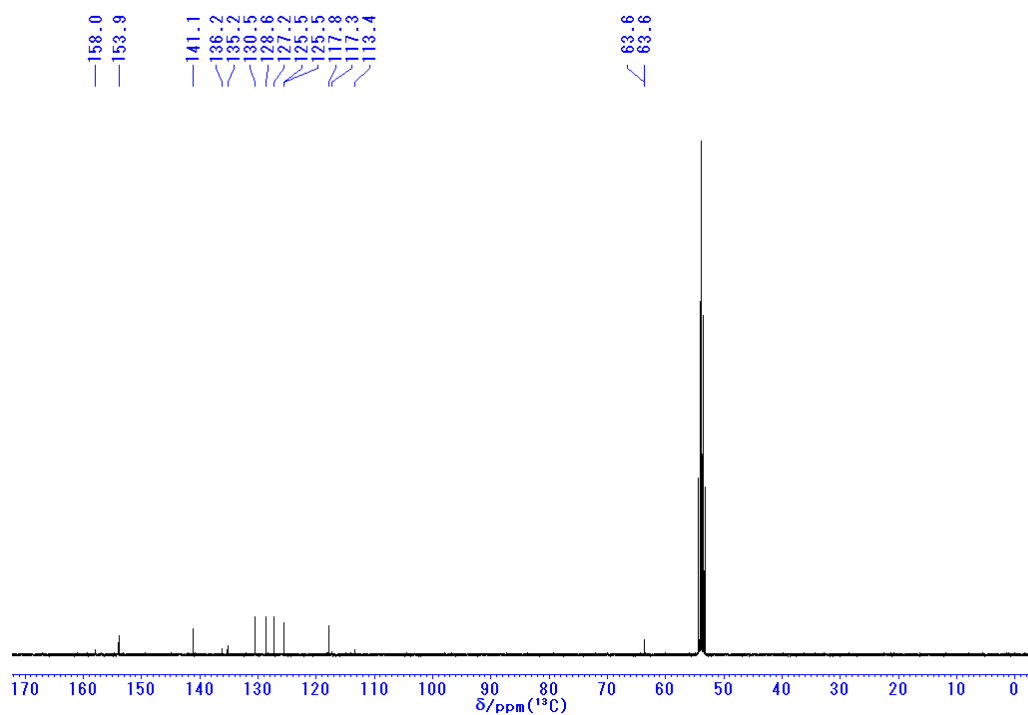


Chart S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **BAmF-Br**, CD_2Cl_2 , 100 MHz.

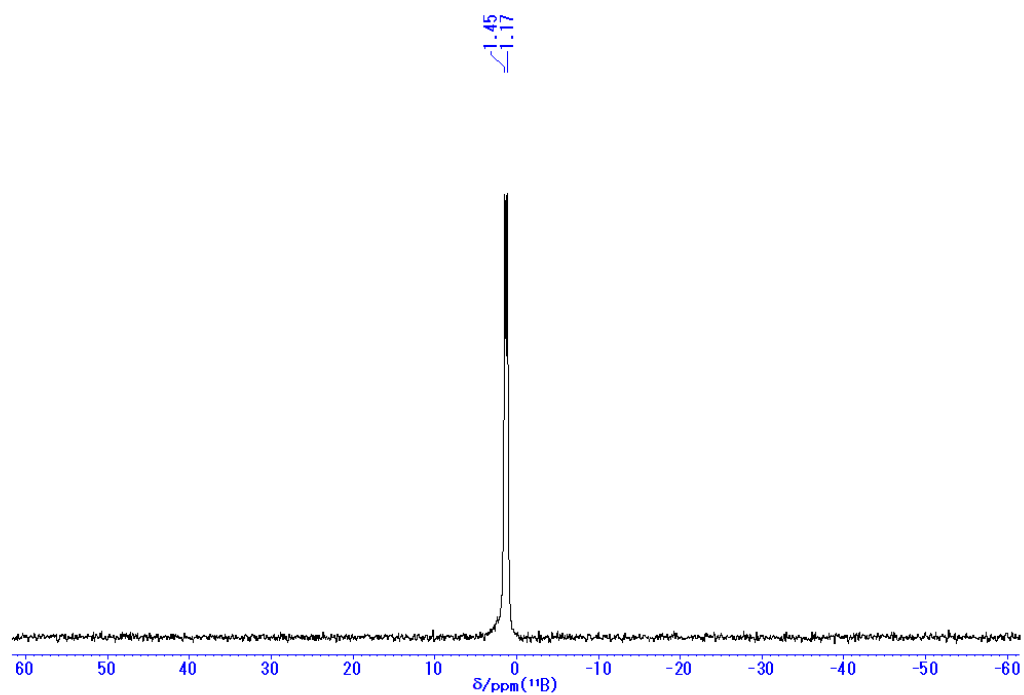
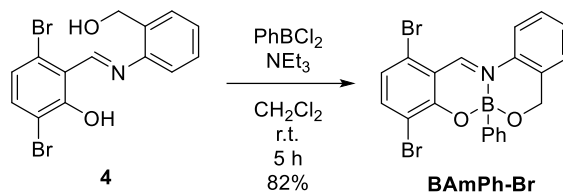


Chart S7. ^{11}B NMR spectrum of **BAmF-Br**, CD_2Cl_2 , 128 MHz.

Synthesis of BAmPh-Br



4 (0.10 g, 0.26 mmol) was dissolved in dry toluene (8 mL) under N_2 atmosphere and triethylamine (0.05 mL, 0.4 mmol) was then added to the reaction mixture at room temperature. Dichloro(phenyl)borane (0.1 mL, 0.8 mmol) was added and stirred for 5 h at room temperature. The reaction mixture was quenched by EtOH and concentrated by rotary evaporator. Then, the product was extracted with CH_2Cl_2 . Organic layer was washed with brine, dried over MgSO_4 and evaporated to afford **BAmPh-Br** (0.10 g, 0.21 mmol, 82%) as a yellow powder.

^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.95 (s, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.50–7.43 (m, 2H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.19–7.17 (m, 2H), 7.12–7.11 (m, 3H), 7.03 (d, $J = 8.6$ Hz, 1H), 4.98 (d, $J = 15.2$ Hz, 1H), 4.85 (d, $J = 15.1$ Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) δ 159.1, 155.7, 141.0, 138.5, 136.5, 131.4, 130.0, 128.8, 127.7, 127.7, 127.0, 125.5, 124.6, 118.6, 118.5, 113.6, 63.4 ppm. One carbon peak directly connected at boron was not detected. ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 5.20 ppm. HRMS (ESI) *calcd.* for $\text{C}_{20}\text{H}_{14}\text{BBr}_2\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 491.9377; *found*: 491.9379.

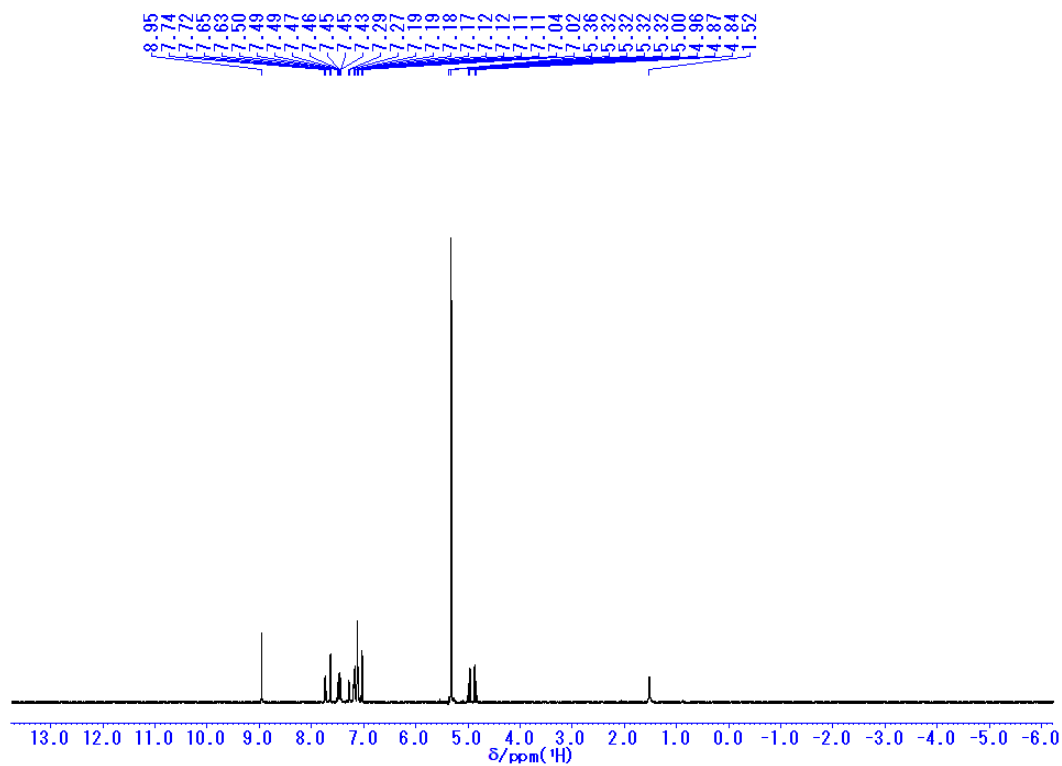


Chart S8. ^1H NMR spectrum of **BAmPh-Br**, CD_2Cl_2 , 400 MHz.

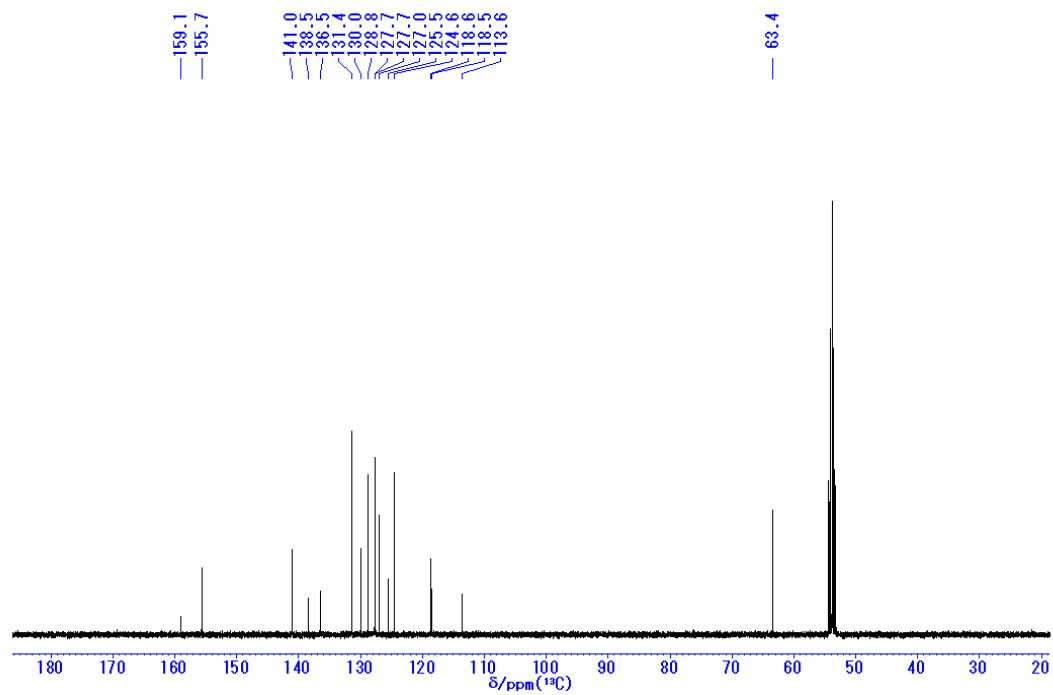


Chart S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **BAmPh-Br**, CD_2Cl_2 , 100 MHz.

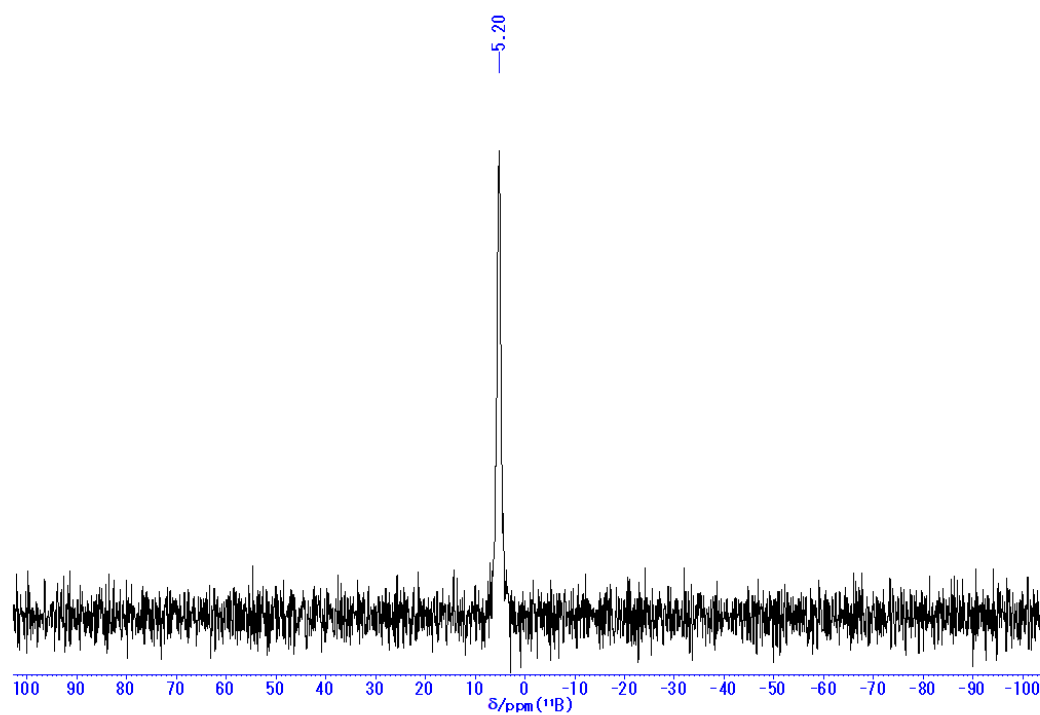
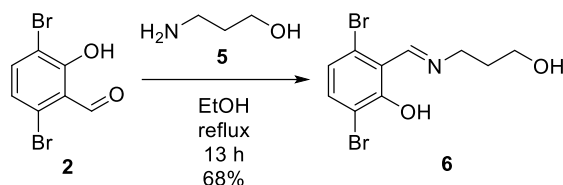


Chart S10. ^{11}B NMR spectrum of **BAmPh-Br**, CD_2Cl_2 , 128 MHz.

Synthesis of **6** ((*E*)-3,6-dibromo-2-(((3-hydroxypropyl)imino)methyl)phenol)



2 (0.59 g, 2.13 mmol) and 3-amino-1-propanol (**5**) (0.16 g, 2.13 mmol) were dissolved in EtOH (10 mL) under N₂ atmosphere and refluxed for 13 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by reprecipitation (good solvent: CHCl₃, poor solvent: hexane) to afford **6** (0.49 g, 1.45 mmol, 68%) as an orange powder.

¹H NMR (CDCl₃, 400 MHz), δ 15.77 (br, 1H), 8.69 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H) 3.85–4.79 (m, 4H), 2.04–1.97 (m, 2H) 1.56 (s, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz), δ 166.8, 165.2, 137.2, 124.6, 120.4, 115.0, 114.8, 59.4, 51.7, 32.4 ppm. HRMS (ESI) calcd. for C₁₀H₁₂Br₂NO₂ [M+H]⁺: 335.9229; found: 335.9233.

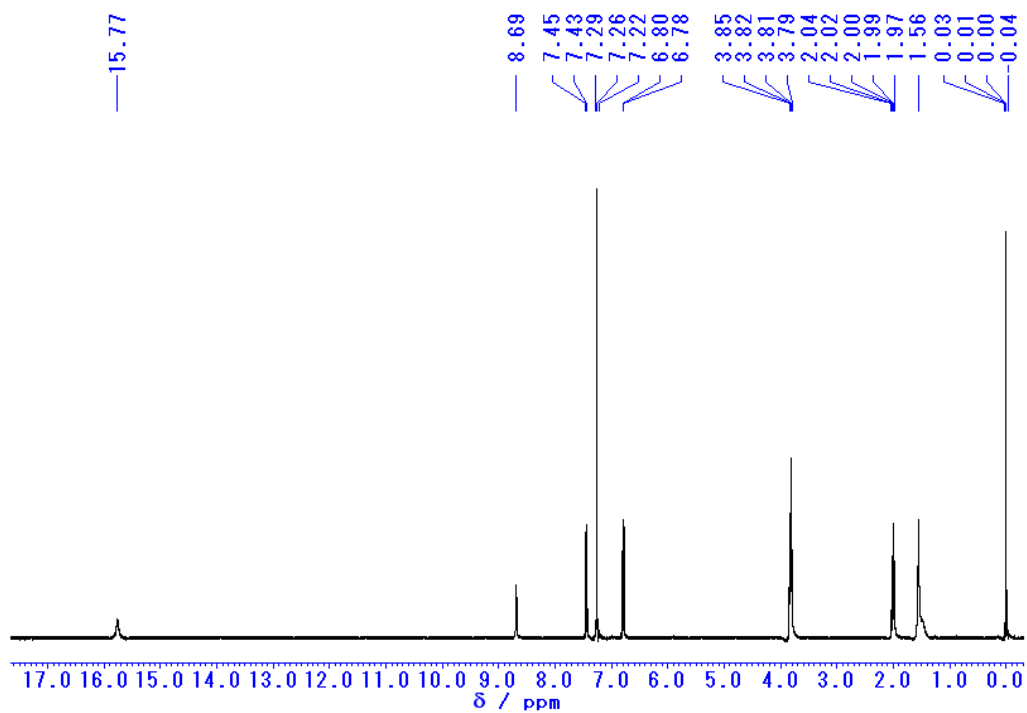


Chart S11. ^1H NMR spectrum of **6**, CDCl_3 , 400 MHz.

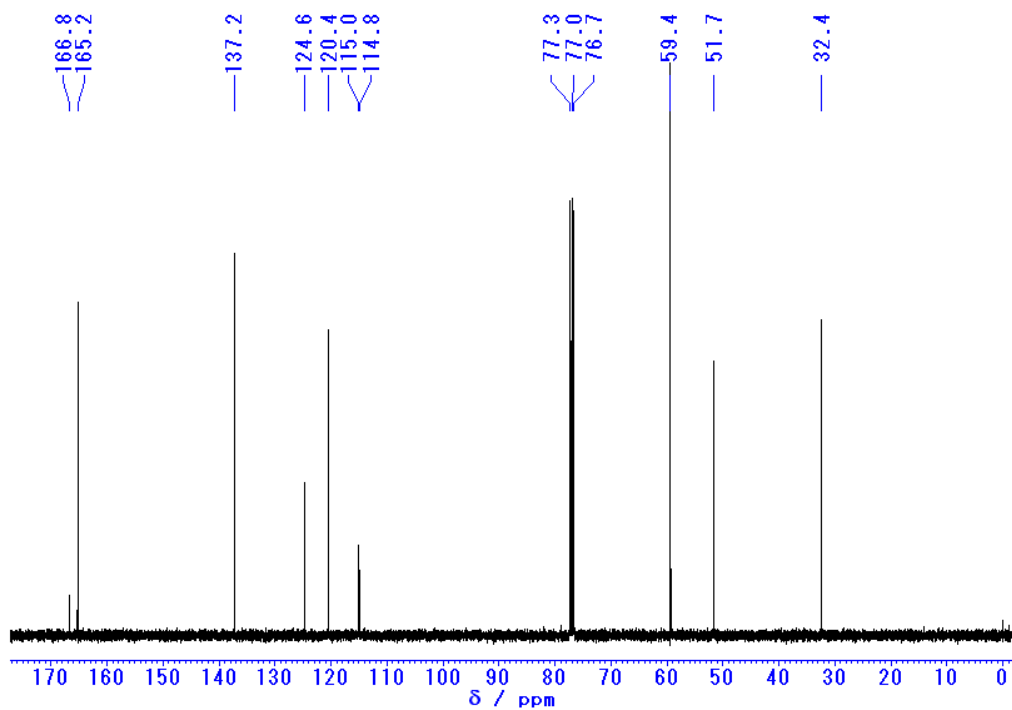
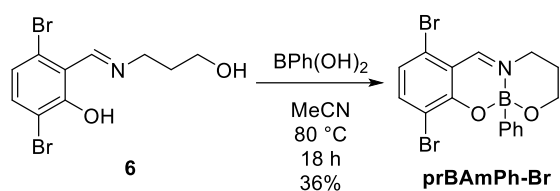


Chart S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6**, CDCl_3 , 100 MHz.

Synthesis of prBAmPh-Br



6 (0.15 g, 0.44 mmol) and phenylboronic acid (0.21 g, 1.75 mmol) was dissolved in dry MeCN (9 mL) under N₂ atmosphere. The solution was stirred for 18 h at 80 °C. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was washed with Et₂O and purified by recrystallization (good solvent: CHCl₃, poor solvent: hexane) to afford **prBAmPh-Br** (0.068 g, 0.16 mmol, 36%) as a pale yellow powder.

¹H NMR (CD₂Cl₂, 400 MHz) δ 8.61 (d, J = 1.68 Hz 1H), 7.53 (d J = 8.3 Hz, 1H), 7.37–7.35 (m, 2H), 7.30–7.21 (m, 3H), 6.95 (d, J = 8.3 Hz, 1H), 4.07–4.00 (m, 2H), 3.93 (td, J = 11.3, 2.76 Hz, 1H), 3.87–3.83 (m, 1H), 2.20–2.09 (m, 1H), 1.88–1.83 (m, 1H) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz) δ 160.0, 158.3, 140.5, 131.5, 128.1, 127.8, 124.7, 123.7, 116.2, 113.4, 61.5, 56.4, 31.0 ppm. One carbon peak directly connected at boron was not detected. ¹¹B NMR (CD₂Cl₂, 128 MHz) δ 4.91 ppm. HRMS (ESI) calcd. for C₁₆H₁₄BBBr₂NO₂Na [M+Na]⁺: 443.9377; found: 443.9369.

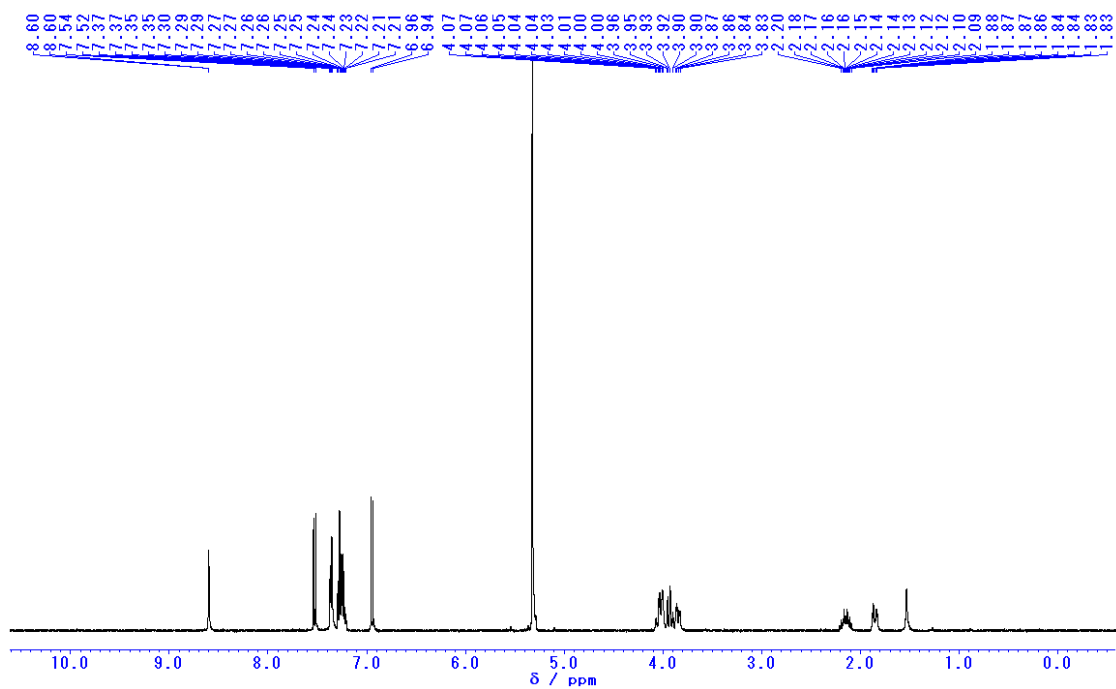


Chart S13. ^1H NMR spectrum of **prBAmPh-Br**, CD_2Cl_2 , 400 MHz.

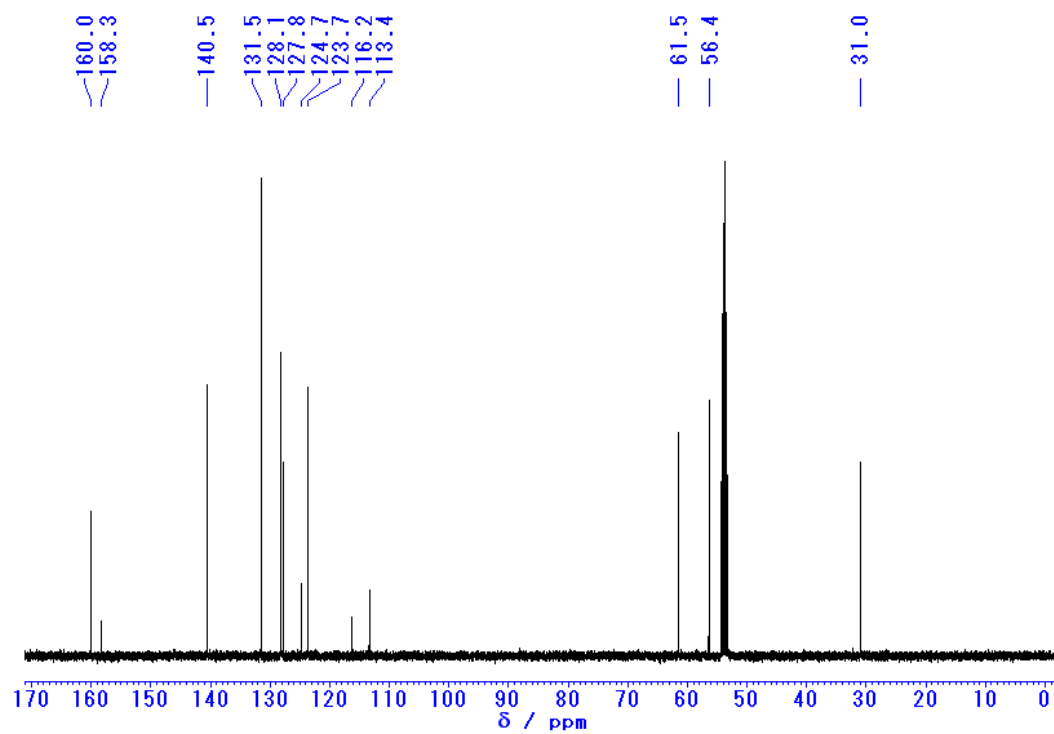


Chart S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **prBAmPh-Br**, CD_2Cl_2 , 128 MHz.

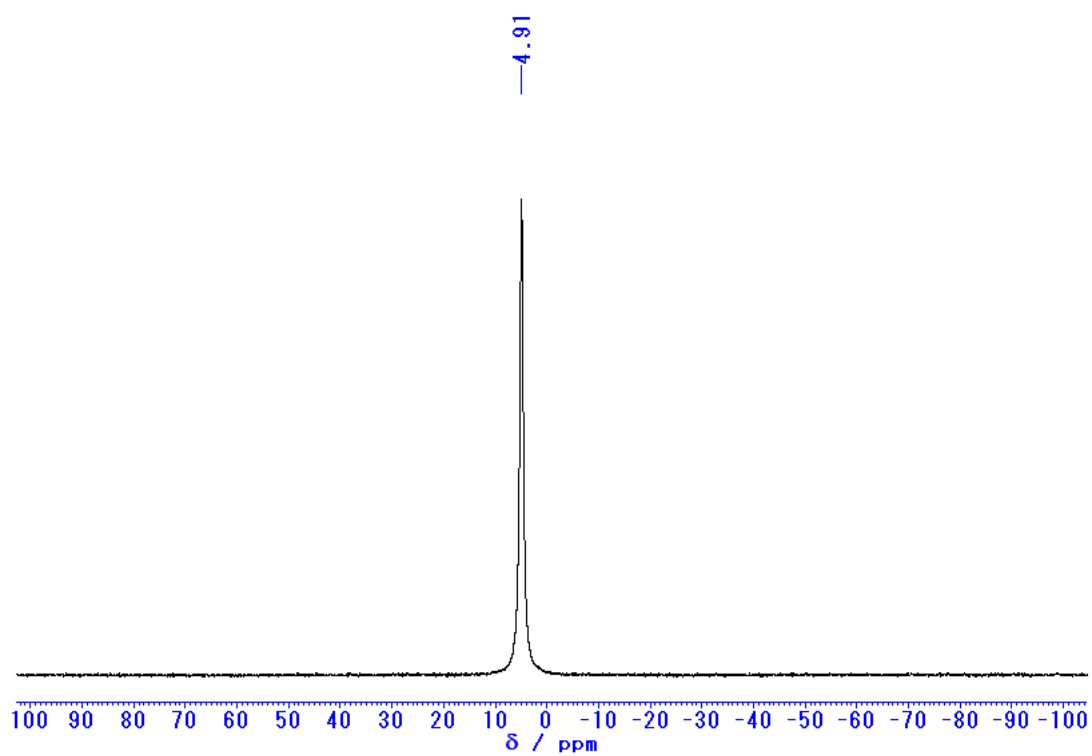
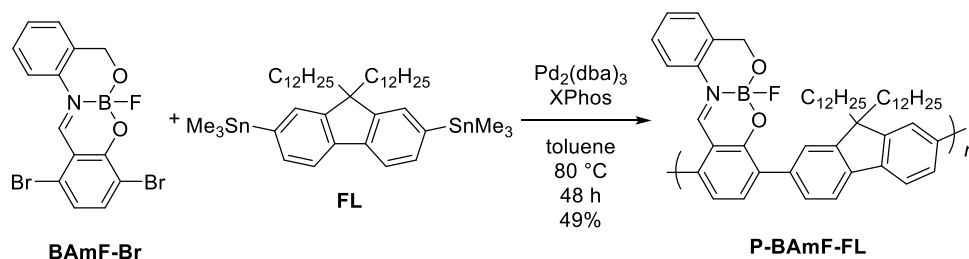


Chart S15. ^{11}B NMR spectrum of **prBAmPh-Br**, CD_2Cl_2 , 128 MHz.

Synthesis of P-BAmF-FL



The mixture of **BAmF-Br** (29.9 mg, 0.073 mmol), (9,9-didodecyl-9H-fluorene-2,7-diyl)bis(trimethylstannane) (60.1 mg, 0.073 mmol), $\text{Pd}_2(\text{dba})_3$ (2.0 mg, 0.0022 mmol), XPhos (2.1 mg, 0.0044 mmol) in toluene (1.5 mL) was stirred at 80 °C for 48 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-BAmF-BT** (27 mg, 49%) as an orange solid.

$M_n = 10,300$, $M_w = 15,700$, $M_w/M_n = 1.5$. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.90 (s, 1H), 8.07–7.83 (m, 3H), 7.78–7.74 (d, 2H), 7.70–7.55 (m, 2H), 7.45–7.25 (m, 6H), 2.13 (br, 4H), 1.39–0.84 (m, 46H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) 158.2, 151.9, 151.7, 138.3, 136.9, 135.0, 129.3, 129.3, 128.4, 127.2, 127.1, 124.7, 122.2, 120.2, 117.0, 116.4, 63.4, 40.7, 32.3, 32.3, 30.7, 30.5, 30.1, 30.0, 29.9, 29.9, 29.7, 29.7, 24.6, 23.1, 14.3 ppm. ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 0.98 ppm.

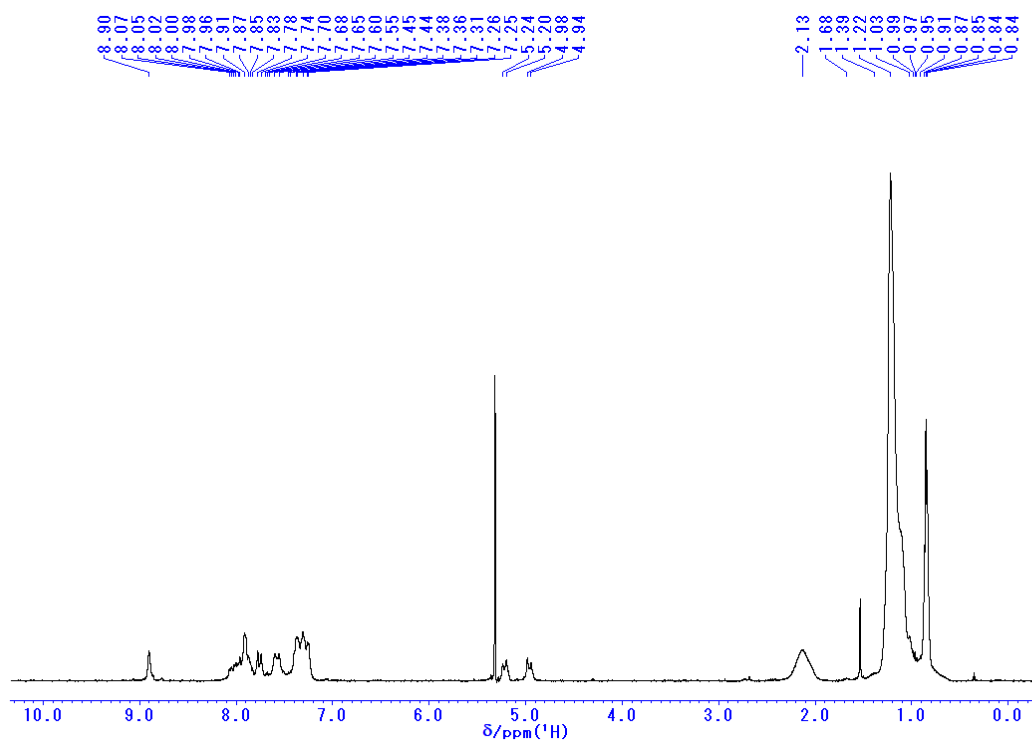


Chart S16. ^1H NMR spectrum of **P-BAmF-FL**, CD_2Cl_2 , 400 MHz.

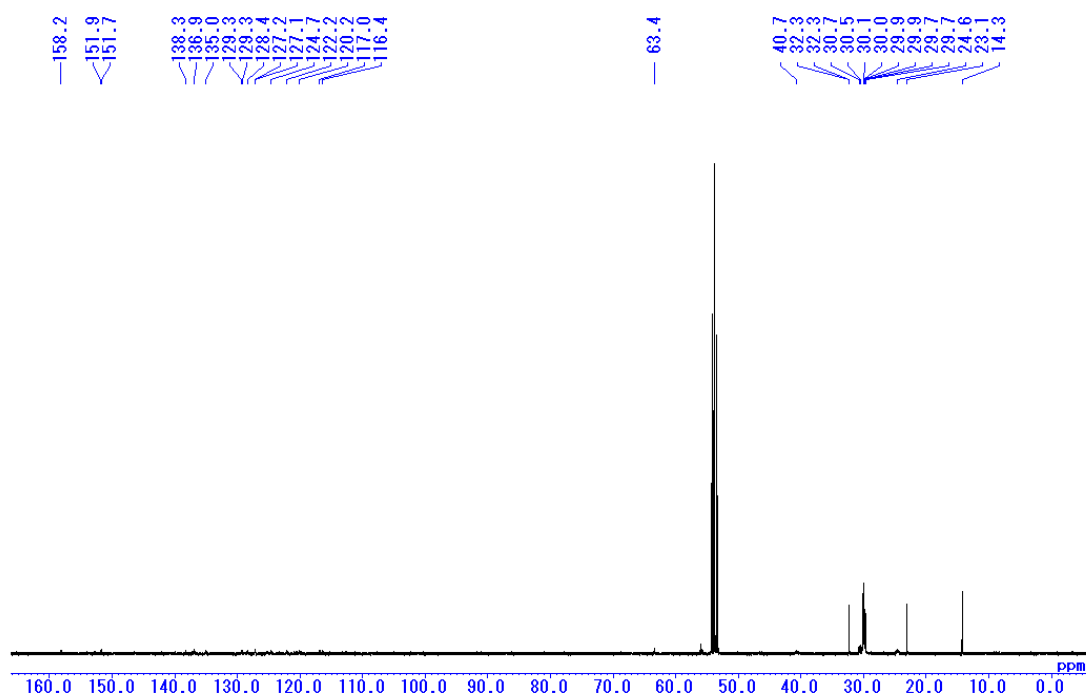


Chart S17. ^{13}C NMR spectrum of **P-BAmF-FL**, CD_2Cl_2 , 100 MHz.

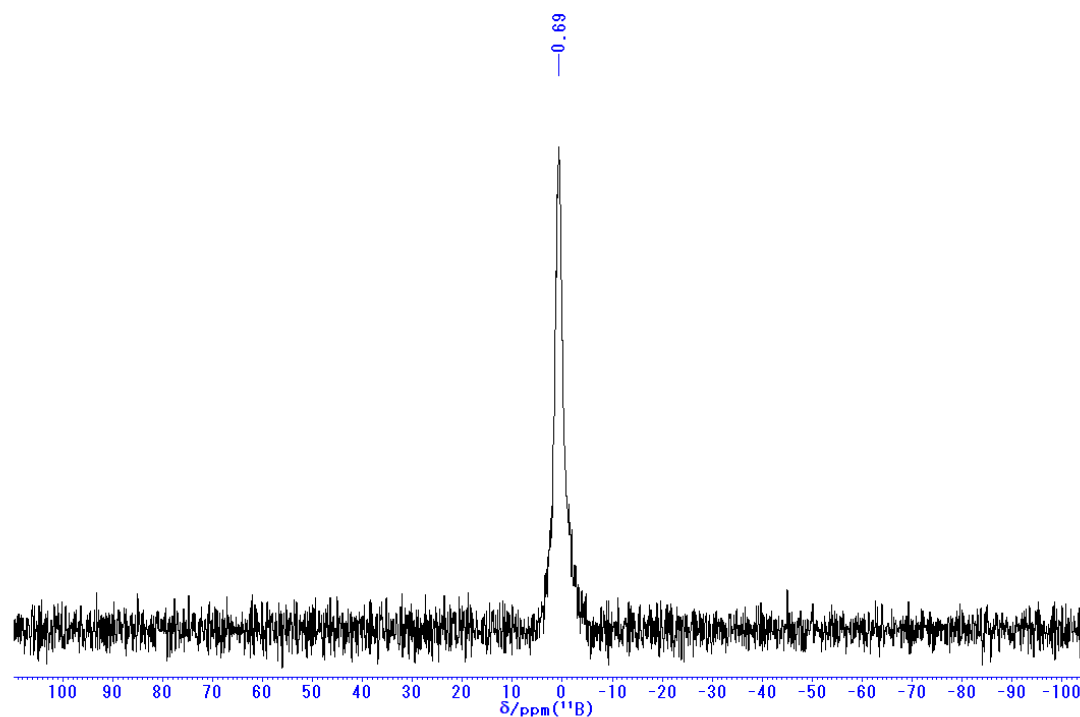


Chart S18. ^{11}B NMR spectrum of **P-BAmF-FL**, CD_2Cl_2 , 128 MHz.

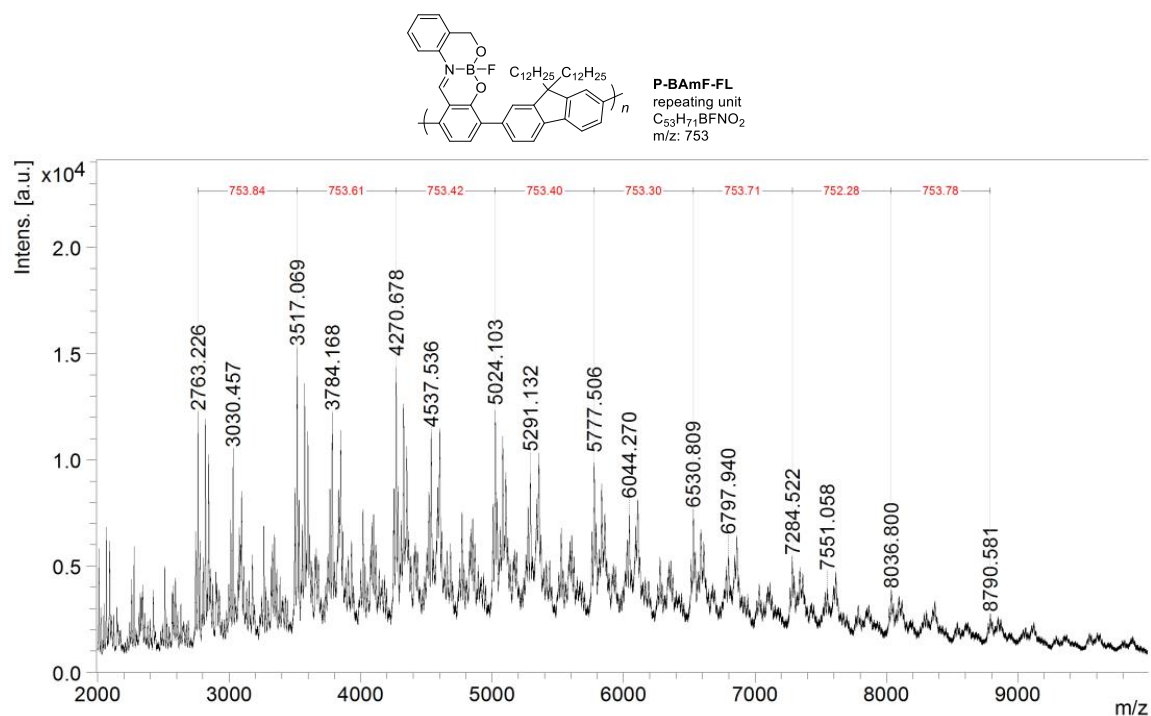
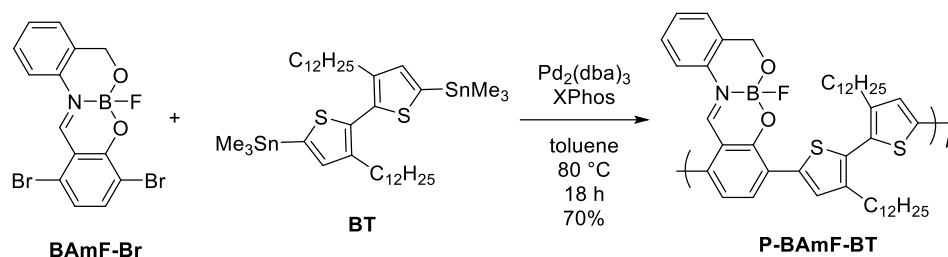


Chart S19. MALDI-TOF mass spectrum of **P-BAmF-FL**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-BAmF-BT



The mixture of **BAmF-Br** (19.4 mg, 0.047 mmol), 5,5'-bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene (38.9 mg, 0.047 mmol), $\text{Pd}_2(\text{dba})_3$ (1.3 mg, 0.0014 mmol) and XPhos (1.3 mg, 0.0028 mmol) in toluene (1.0 mL) was stirred at 80 °C for 18 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-BAmF-BT** (24.7 mg, 70%) as a red solid.

$M_n = 20,800$, $M_w = 39,100$, $M_w/M_n = 1.9$. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 9.12 (s, 1H), 8.02 (br, 1H), 7.70–7.50 (m, 2H), 7.34 (br, 2H), 7.22 (br, 2H), 7.10–7.06 (m, 1H), 5.21–5.16 (m, 1H), 4.97–4.93 (m, 1H), 2.64 (br, 4H), 1.64 (br, 4H), 1.17 (br, 36H), 0.79–0.76 (br, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) 32.3, 32.3, 30.1, 30.1, 30.1, 30.0, 30.0, 29.9, 29.8, 23.1, 14.3 ppm. The other $^{13}\text{C}\{^1\text{H}\}$ signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2 , 128 MHz), δ 0.87 (d, $J = 28.2$ Hz) ppm.

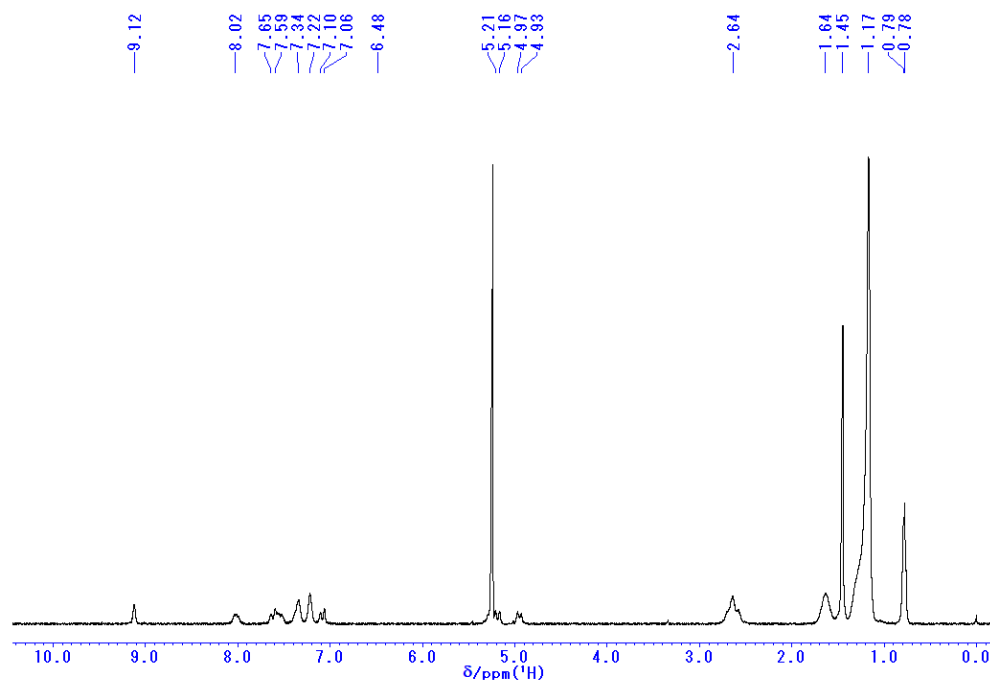


Chart S20. ^1H NMR spectrum of **P-BAmF-BT**, CD_2Cl_2 , 400 MHz.

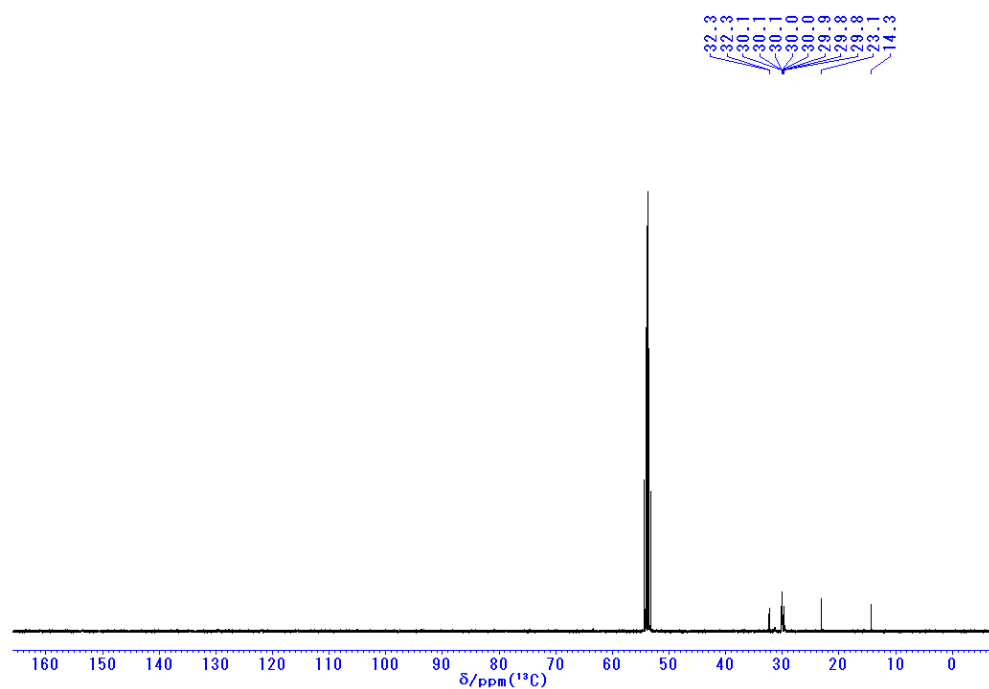


Chart S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P-BAmF-BT**, CD_2Cl_2 , 100 MHz.

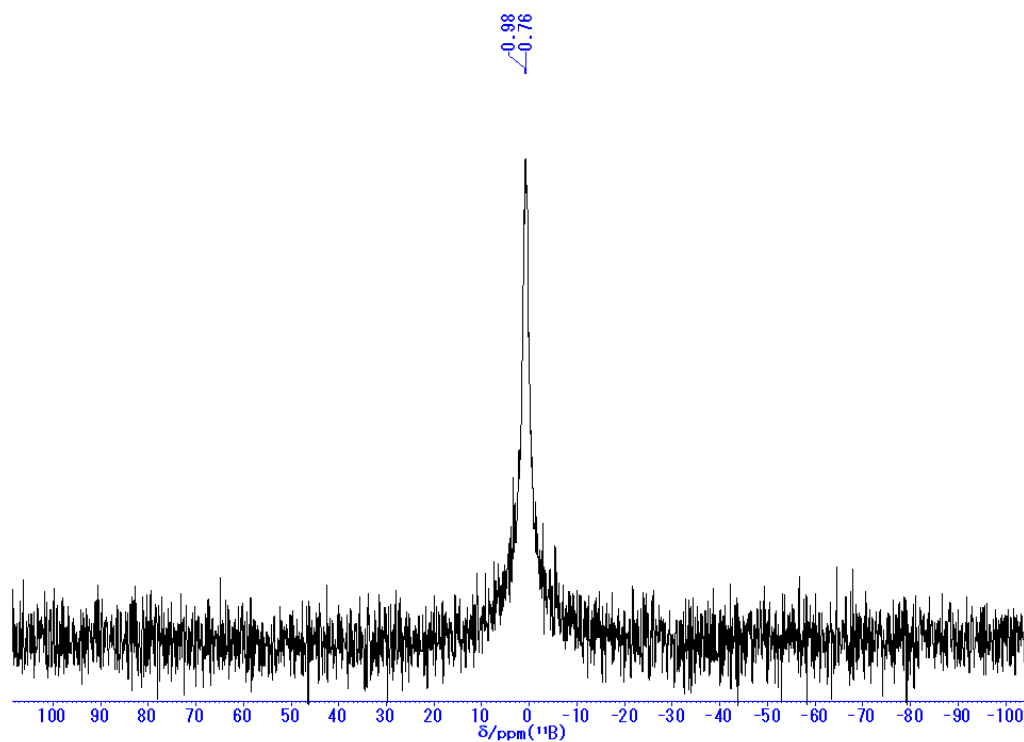


Chart S22. ^{11}B NMR spectrum of **P-BAmF-BT**, CD_2Cl_2 , 128 MHz.

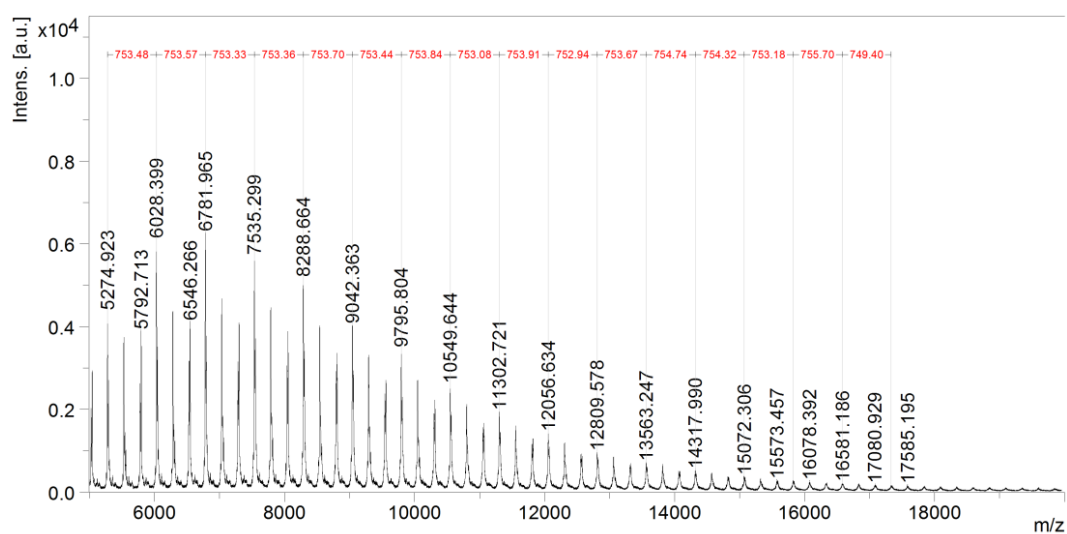
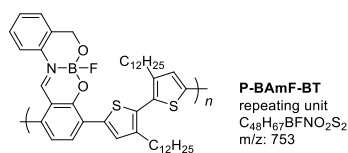
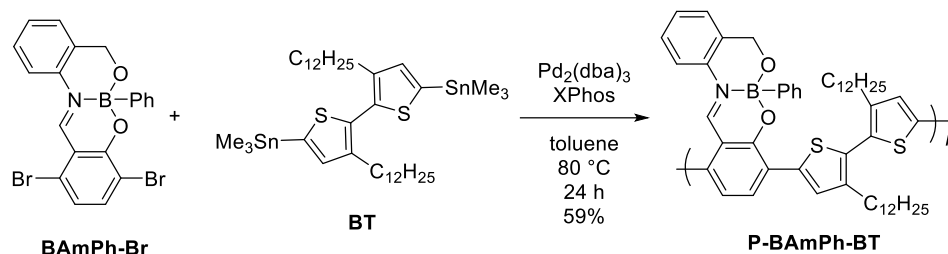


Chart S23. MALDI-TOF mass spectrum of **P-BAmF-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-BAmPh-BT



The mixture of **BAmPhBr** (34.1 mg, 0.072 mmol), 5,5'-Bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene (60.0 mg, 0.072 mmol), $\text{Pd}_2(\text{dba})_3$ (2.0 mg, 0.0022 mmol), XPhos (2.1 mg, 0.0044 mmol) in toluene (1.5 mL) was stirred at 80 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **p-BAmPh-BT** (34.6 mg, 59%) as a red solid.

$M_n = 16,900$, $M_w = 29,800$, $M_w/M_n = 1.8$. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 9.05 (s, 1H), 8.04–8.02 (m, 1H), 7.76–7.69 (m, 2H), 7.41–7.39 (m, 4H), 7.27 (d, $J = 5.56$ Hz, 1H), 7.20–7.15 (m, 4H), 7.08–7.02 (m, 1H), 5.03–5.00 (m, 1H), 4.85 (d, $J = 14.4$ Hz, 1H), 2.79–7.64 (m, 4H), 1.73 (s, 4H), 1.34–1.24 (m, 36H), 0.90–0.85 (m, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) 157.3, 138.8, 136.4, 131.8, 127.7, 126.9, 125.3, 120.5, 63.3, 32.3, 30.2, 30.1, 30.1, 30.1, 30.0, 30.0, 29.9, 29.8, 23.1, 14.3 ppm. The other $^{13}\text{C}\{^1\text{H}\}$ signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 2.74 ppm.

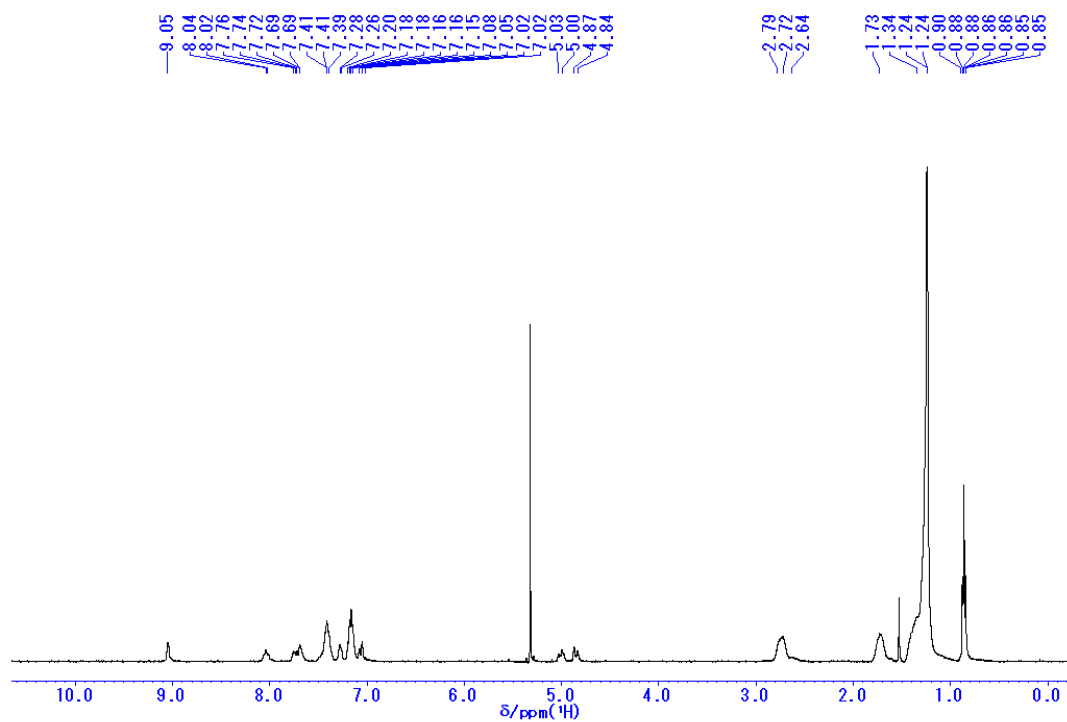


Chart S24. ^1H NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2 , 400 MHz.

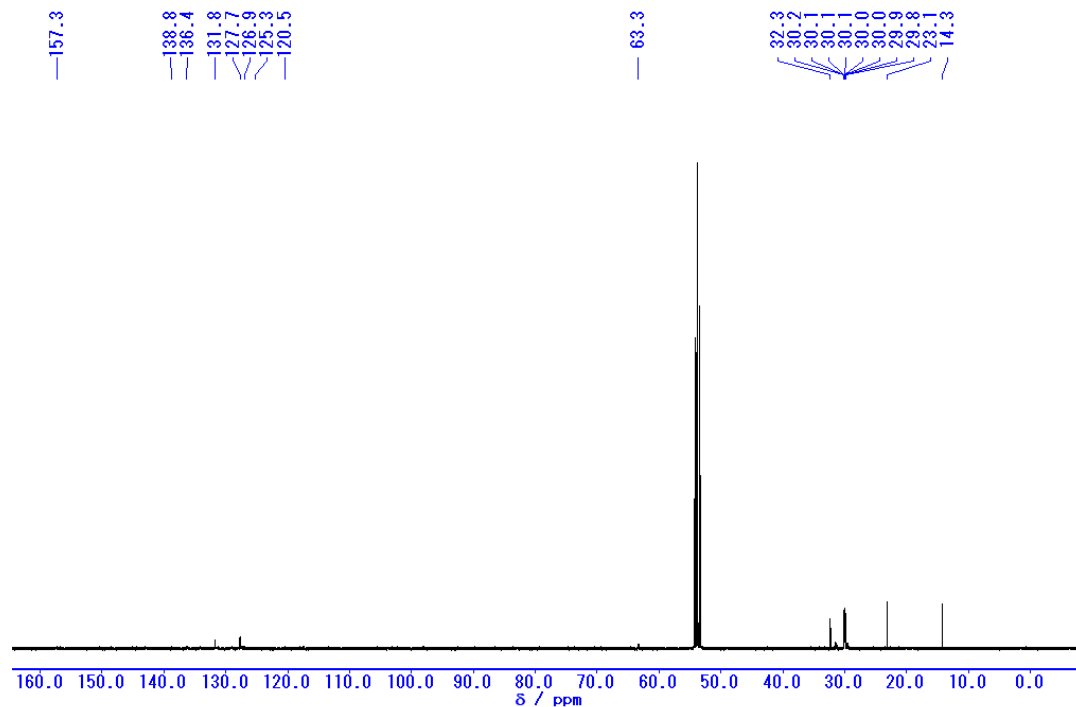


Chart S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2 , 100 MHz.

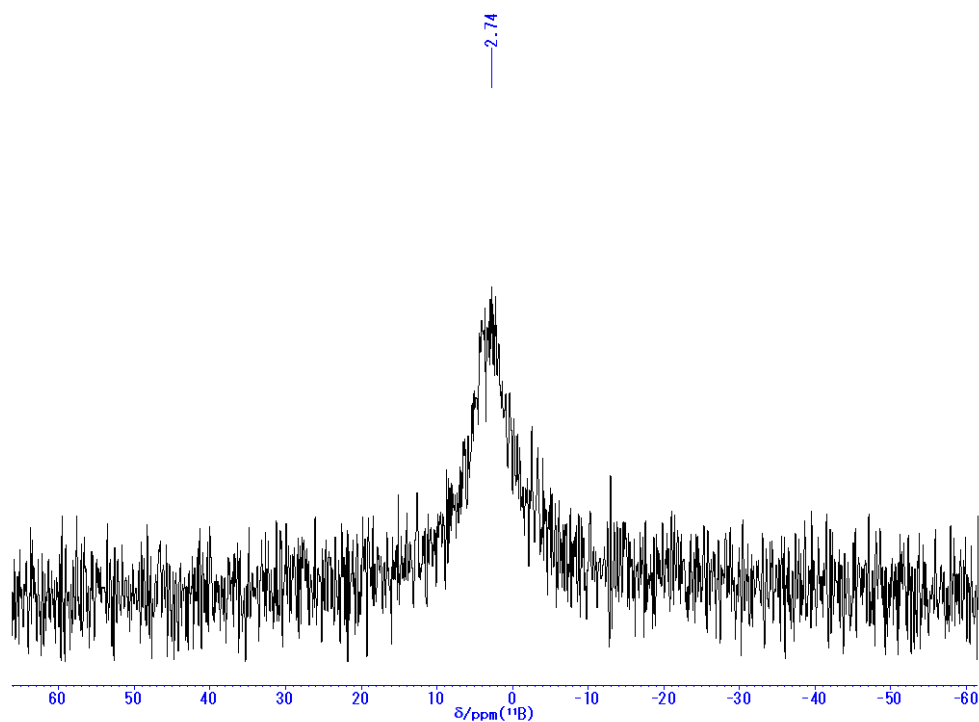


Chart S26. ^{11}B NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2 , 128 MHz.

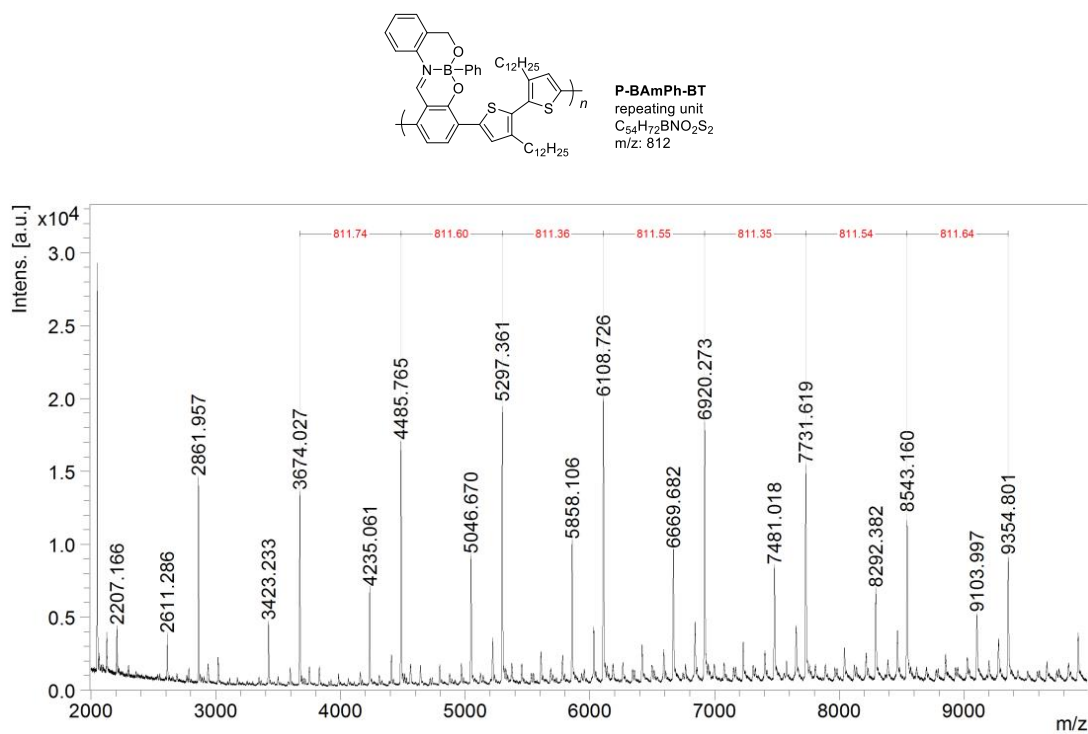
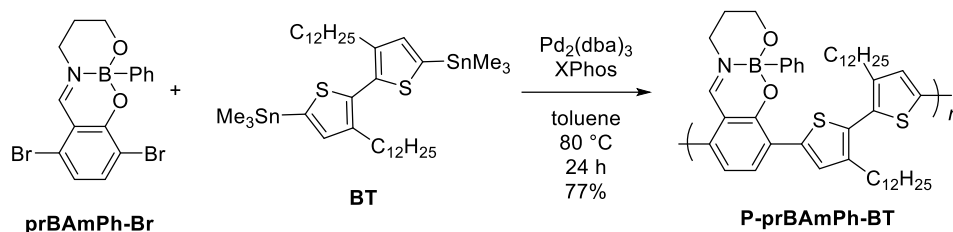


Chart S27. MALDI-TOF mass spectrum of **P-BAmPh-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-prBAmPh-BT



The mixture of **prBAmPhBr** (41.2 mg, 0.097 mmol), 5,5'-Bis(trimethylstannyl)-3,3'-didodecyl-2,2'-bithiophene (80.7 mg, 0.097 mmol), $\text{Pd}_2(\text{dba})_3$ (2.9 mg, 0.0029 mmol), XPhos (2.8 mg, 0.0058 mmol) in toluene (2 mL) was stirred at $80\text{ }^\circ\text{C}$ for 24 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-prBAmPh-BT** (57.4 mg, 77%) as an orange solid.

$M_n = 7,900$, $M_w = 22,400$, $M_w/M_n = 2.8$. ^1H NMR (CD_2Cl_2 , 400 MHz) δ 8.60 (d, $J = 8.08$ Hz, 1H), 7.92–7.87 (m, 1H), 7.55–7.51 (m, 3H), 7.30–7.22 (m, 3H), 7.04–7.01 (m, 2H), 4.08 (br, 2H), 3.88 (br, 2H), 2.72–2.56 (m, 4H), 2.17 (br, 1H), 1.84 (br, 2H), 1.64 (br, 3H) 1.25 (br, 36H), 0.88–0.85 (m, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz) 159.9, 156.7, 142.6, 131.7, 128.1, 127.4, 120.6, 115.3, 115.1, 61.1, 56.0, 32.3, 31.2, 30.1, 30.1, 30.1, 30.0, 29.9, 29.8, 29.5, 23.1, 14.3 ppm. The other $^{13}\text{C}\{^1\text{H}\}$ signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2 , 128 MHz) δ 3.24 ppm.

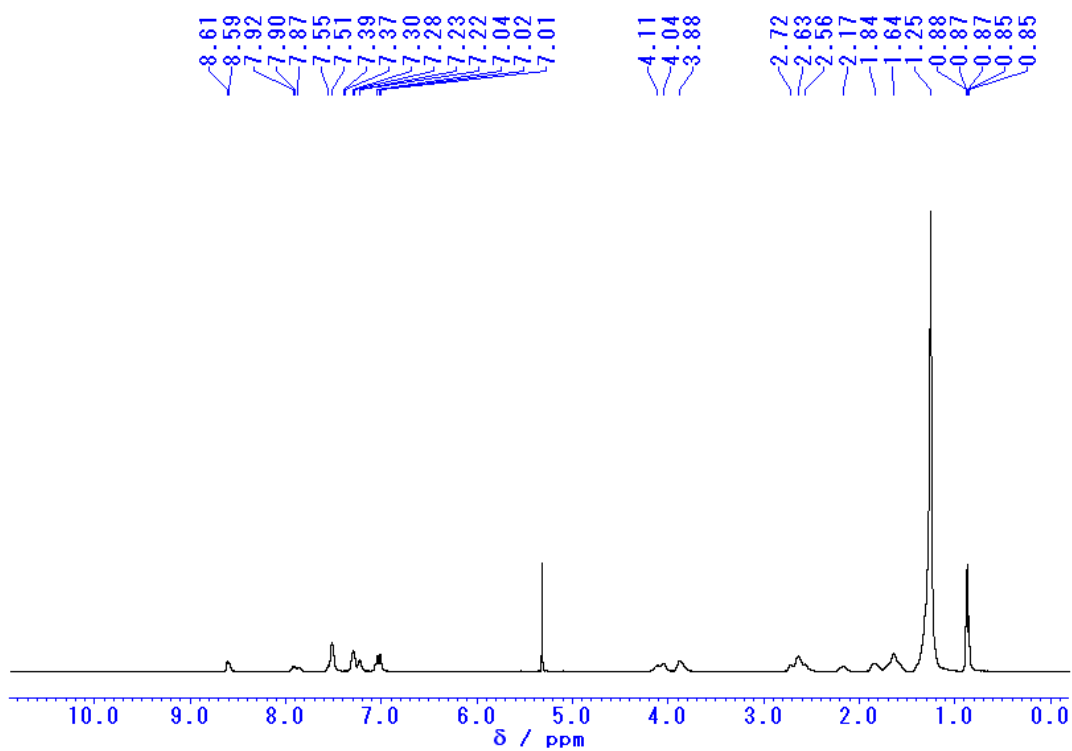


Chart S28. ^1H NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2 , 400 MHz.

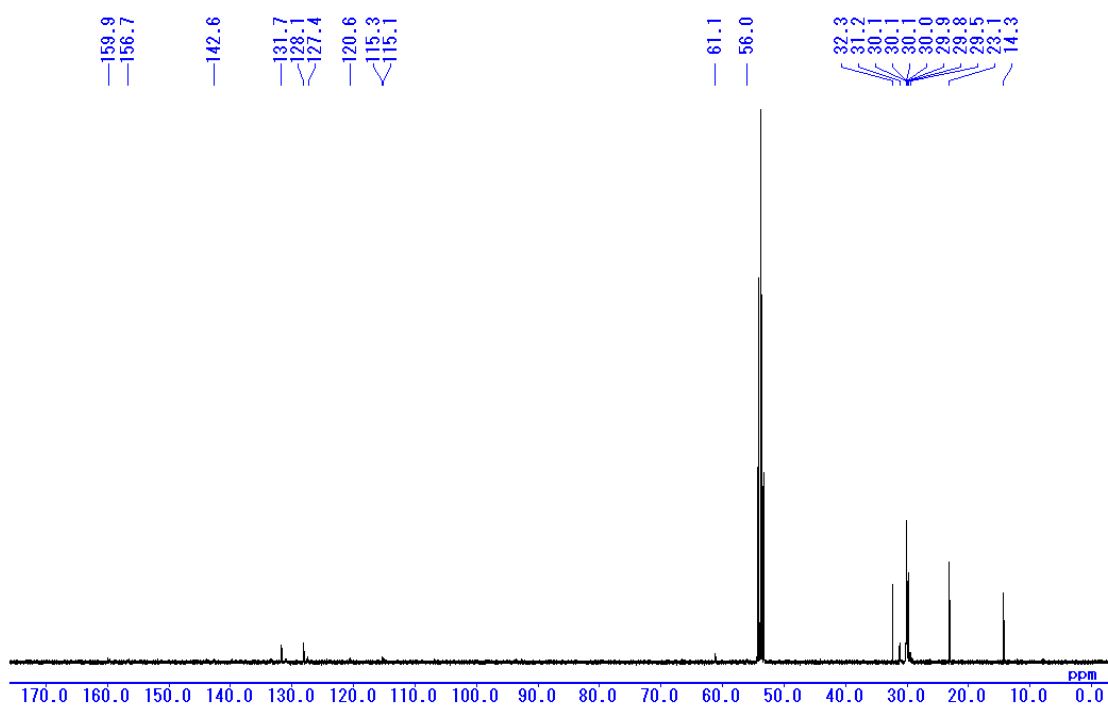


Chart S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2 , 100 MHz.

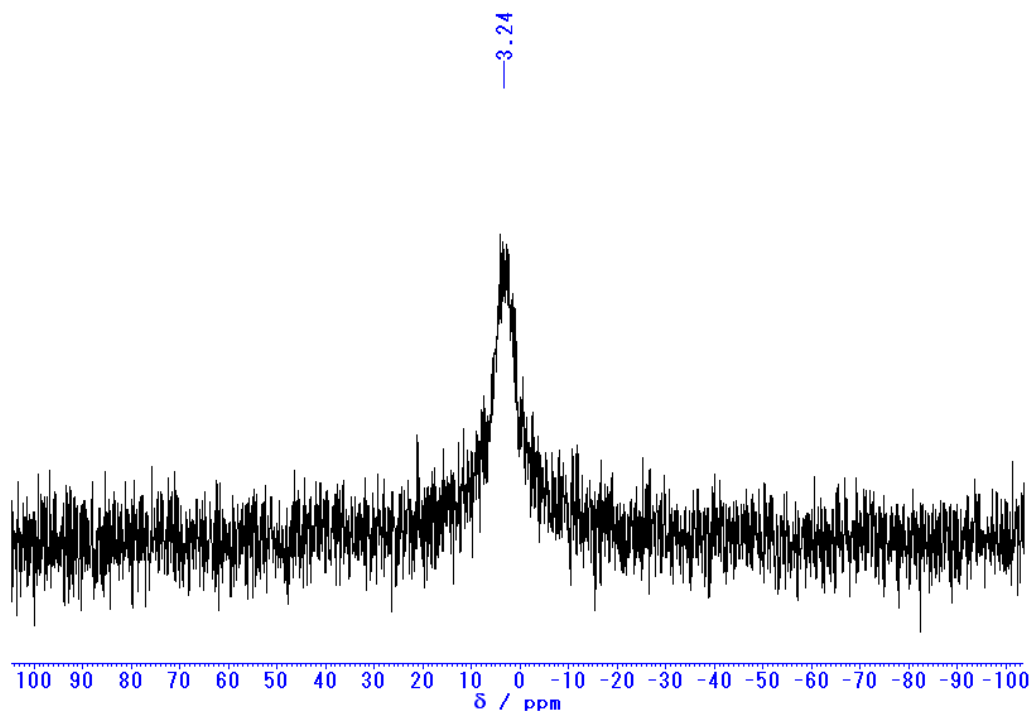


Chart S30. ^{11}B NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2 , 128 MHz.

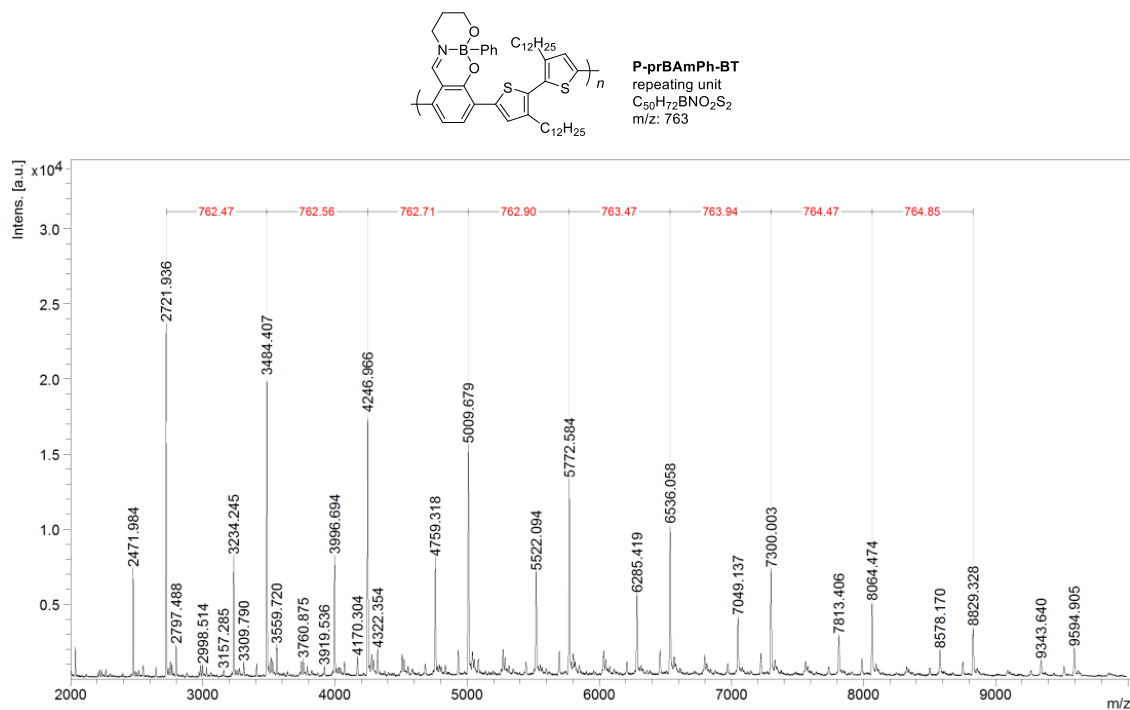
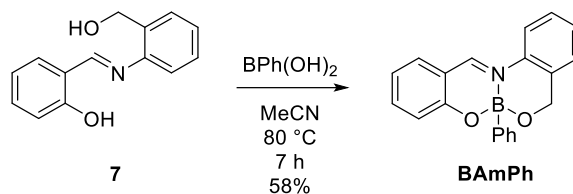


Chart S31. MALDI-TOF mass spectrum of **P-prBAmPh-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of BAmPh



7 (0.20 g, 0.88 mmol) and phenylboronic acid (0.43 g, 3.5 mmol) was dissolved in dry MeCN (18 mL) under N₂ atmosphere. The solution was stirred for 7 h at 80 °C. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was washed with Et₂O and collected by filtration to afford **BAmPh** (0.16 g, 0.51 mmol, 58%) as a yellow solid.

¹H NMR (CD₂Cl₂, 400 MHz) δ 8.65 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.45 (dd, J = 7.8, 1.7 Hz, 1H), 7.41 (dt, J = 8.3, 0.7 Hz, 1H), 7.36 (td, J = 7.4, 1.3 Hz, 1H), 7.24–7.28 (m, 3H), 7.12–7.06 (m, 3H), 7.00 (d, 8.3 Hz, 1H), 6.92–6.88 (m, 1H), 4.98 (d, J = 15.4 Hz, 1H), 4.87 (d, J = 15.4 Hz, 1H) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 100 MHz) δ 161.2, 156.2, 138.8, 138.7, 136.1, 132.6, 131.5, 129.1, 128.4, 127.6, 127.3, 126.8, 120.0, 119.8, 118.0, 117.9, 63.7 ppm. One carbon peak directly connected at boron was not detected. ¹¹B NMR (CD₂Cl₂, 128 MHz) δ 4.91 ppm. HRMS (ESI) calcd. for C₂₀H₁₆BNO₂Na [M+Na]⁺: 336.1166; found: 336.1159.

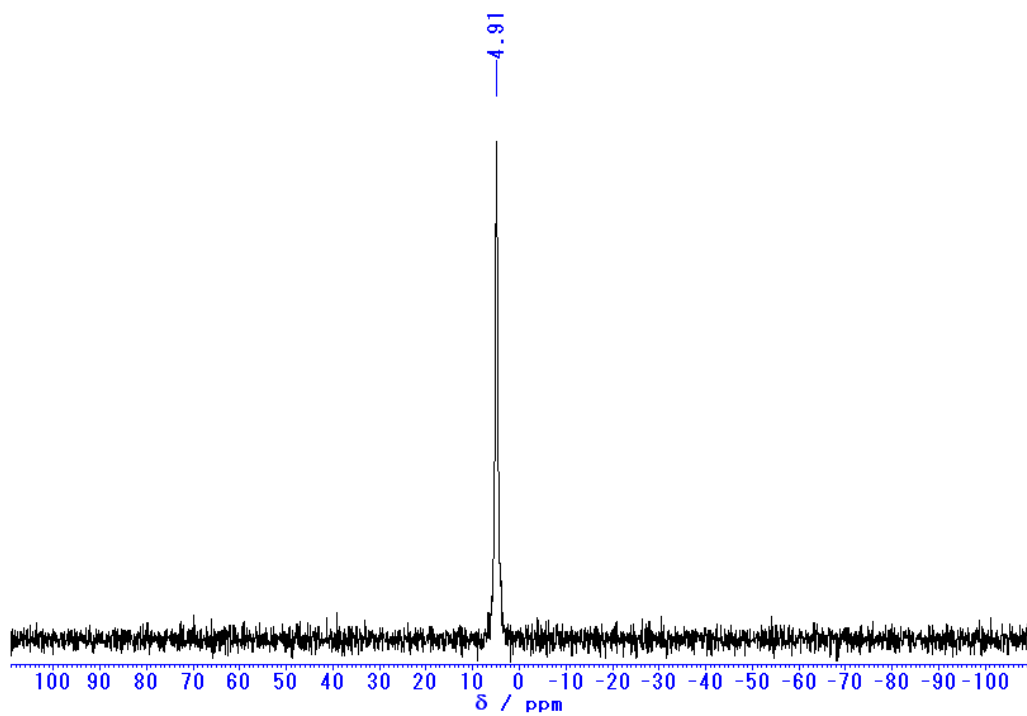
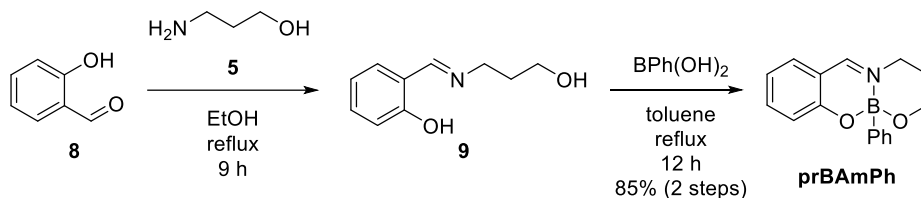


Chart S34. ^{11}B NMR spectrum of **BAmPh**, CD_2Cl_2 , 128 MHz.

Synthesis of prBAmPh



2-Hydroxybenzaldehyde (**8**) (0.50 g, 4.1 mmol) and 3-Amino-1-propanol (**5**) (0.31 g, 4.1 mmol) were dissolved in EtOH (12 mL) and refluxed for 9 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator to afford crude **9**.

Crude **9** (0.72 g, 4.0 mmol) and phenylboronic acid (0.57 g, 4.0 mmol) was dissolved in toluene (20 mL). The solution was refluxed for 12 h. Then, the mixture was cooled to room temperature and collected by filtration to afford **prBAmPh** (0.92 g, 3.5 mmol, 85% (2 steps)) as a white solid.

¹H NMR (CD₂Cl₂, 400 MHz) δ 8.18 (d, J = 1.2 Hz, 1H), 7.43–7.38 (m, 1H), 7.36–7.31 (m, 3H), 7.28–7.23 (m, 2H), 7.19 (tt, J = 7.2, 1.9 Hz, 1H), 6.82 (ddd, J = 7.7, 7.2, 1.0 Hz, 1H), 6.78–6.75 (m, 1H), 4.00–3.88 (m, 3H), 3.72–3.68 (m, 1H), 2.18–2.06 (m, 1H), 1.79–1.73 (m, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz), δ 160.8, 160.2, 138.0 131.7, 131.5, 128.1, 127.3, 119.6, 118.9, 116.1, 61.8, 56.0, 31.4 ppm. One carbon peak directly connected at boron was not detected. ¹¹B NMR (CD₂Cl₂, 128 MHz) δ 4.71 ppm. HRMS (ESI) calcd for C₁₆H₁₇BNO₂ [M+H]⁺: 288.1166; found: 288.1163.

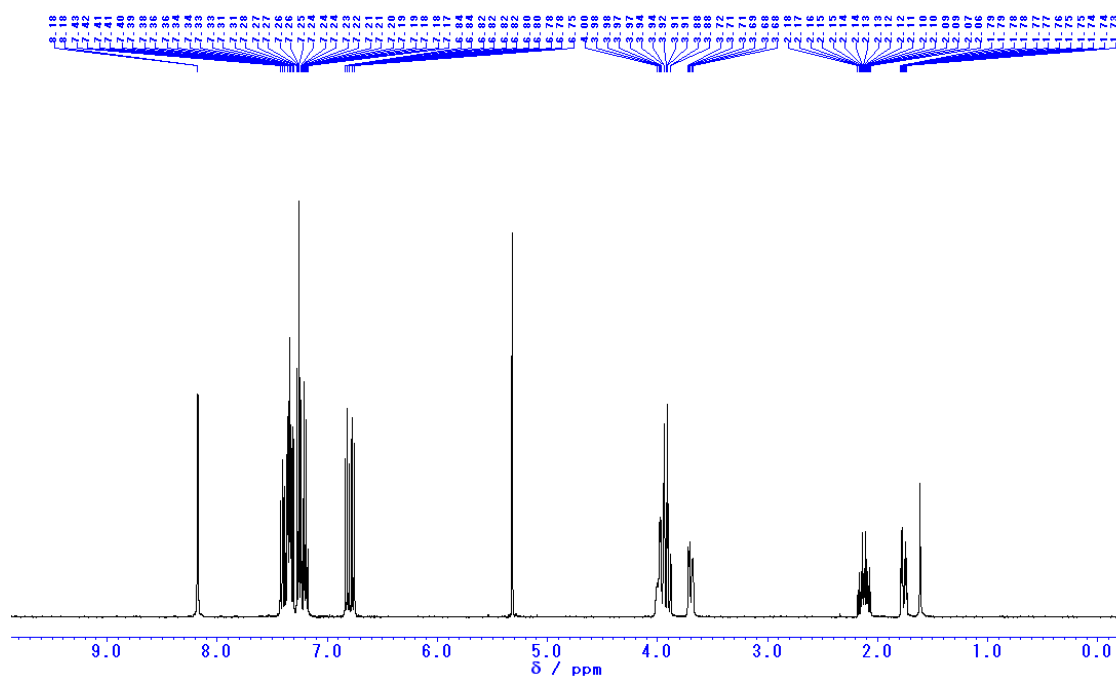


Chart S35. ^1H NMR spectrum of **prBAmPh**, CD_2Cl_2 , 400 MHz.

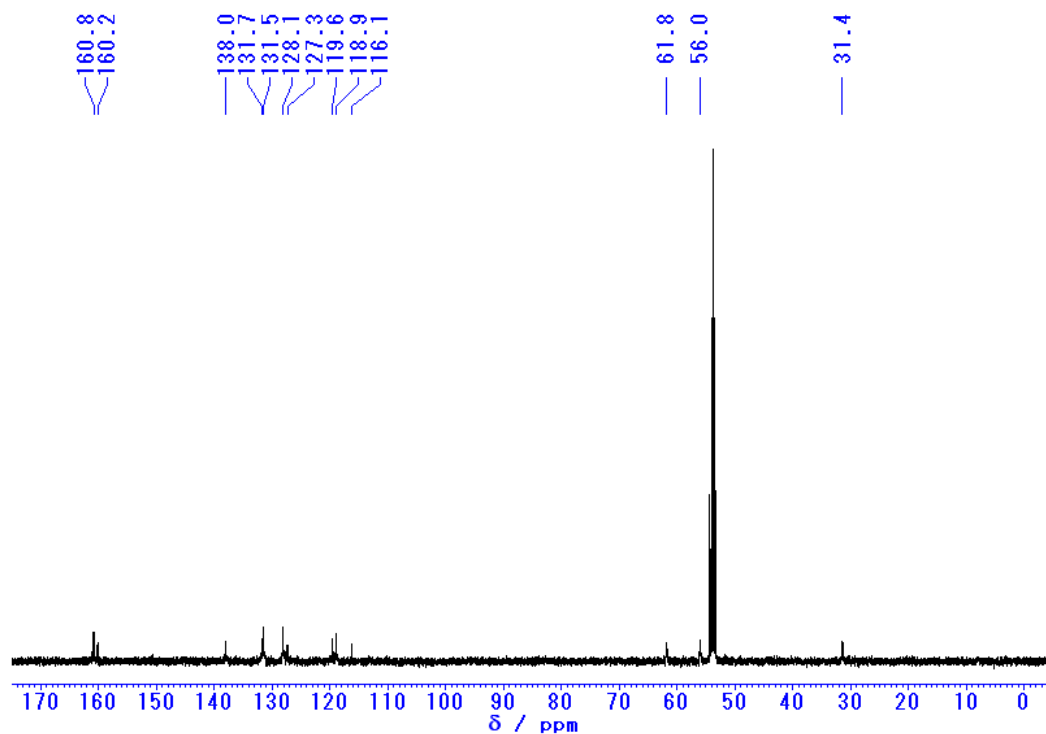


Chart S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **prBAmPh**, CD_2Cl_2 , 100 MHz.

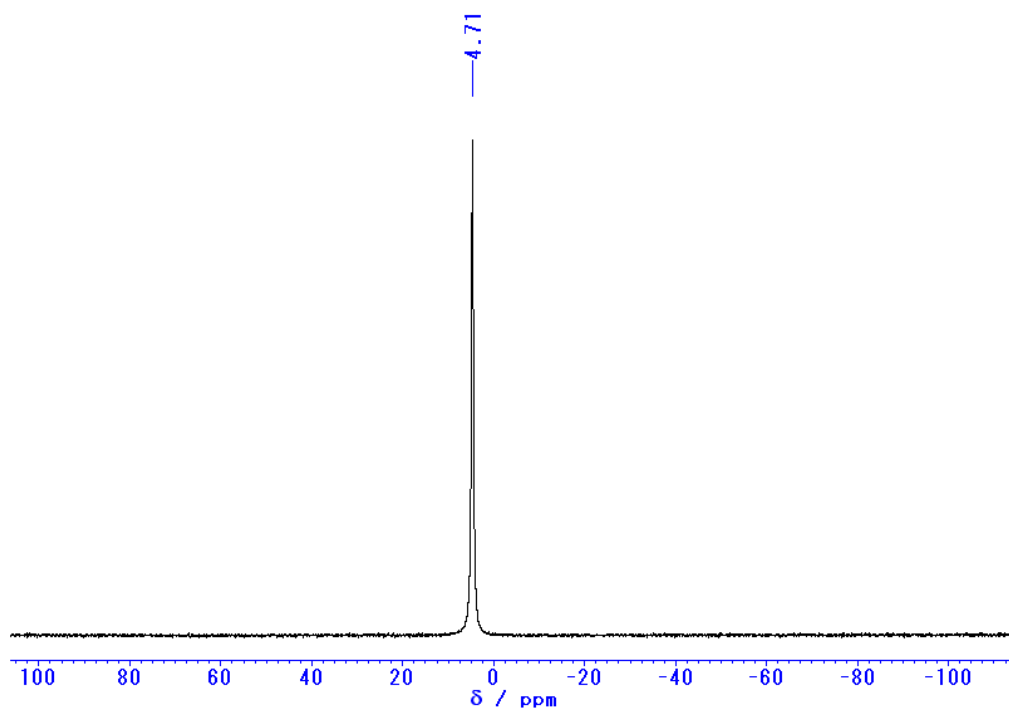


Chart S37. ^{11}B NMR spectrum of **prBAmPh**, CD_2Cl_2 , 128 MHz.

Polymer properties depending on the connection positions

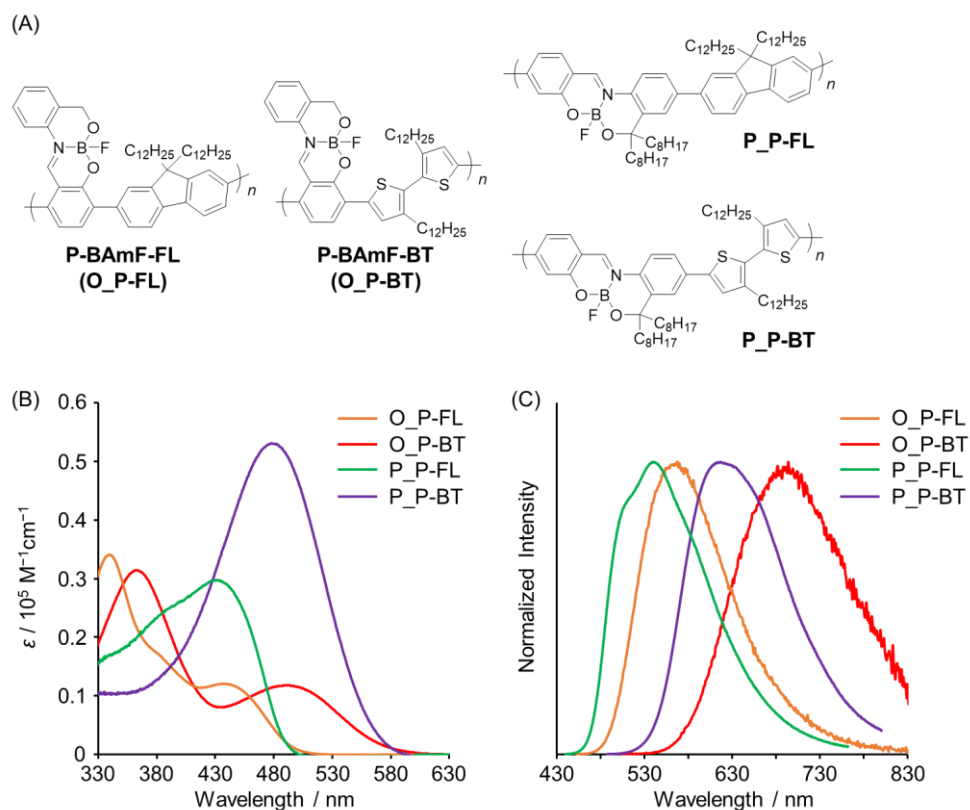


Figure S1. Optical properties of P-BAmF derivatives depending on the connection positions. (A) Chemical structures of P-BAmF derivatives. (B) UV-vis absorption spectra and (C) PL spectra in toluene (1.0×10^{-5} M per repeating unit) and in toluene/ $\text{CHCl}_3 = 99/1$ v/v (1.0×10^{-5} M per repeating unit), excited at wavelengths of absorption maxima for PL. The data of **P_P-FL** and **P_P-BT** are cited from ref 4.

Table S1. Optical data and energy levels of molecular orbitals of P-BAmF derivatives

	λ_{abs}^a /nm	λ_{PL}^a /nm	$\Phi_{\text{PL}}^{a,b}$ /%	$\lambda_{\text{abs,edge}}^a$ /nm	E_{LUMO}^c /eV	E_{HOMO}^c /eV
P_O-FL	437	568	18	496	-3.09	-5.59
P_O-BT	491	694	4	575	-3.24	-5.40
P_P-FL ^d	432	538	22	490	-3.18	-5.71
P_P-BT ^d	479	613	51	562	-3.31	-5.51

^a 1.0×10^{-5} M per repeating unit in toluene, excited at wavelengths of absorption maxima for PL.

^b Absolute PL quantum yield, excited at wavelengths of absorption maxima.

^c $E_{\text{g,opt}} = 1240/\lambda_{\text{abs,edge}}$. $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g,opt}}$.

^d From ref 4.

PL lifetime decay curves

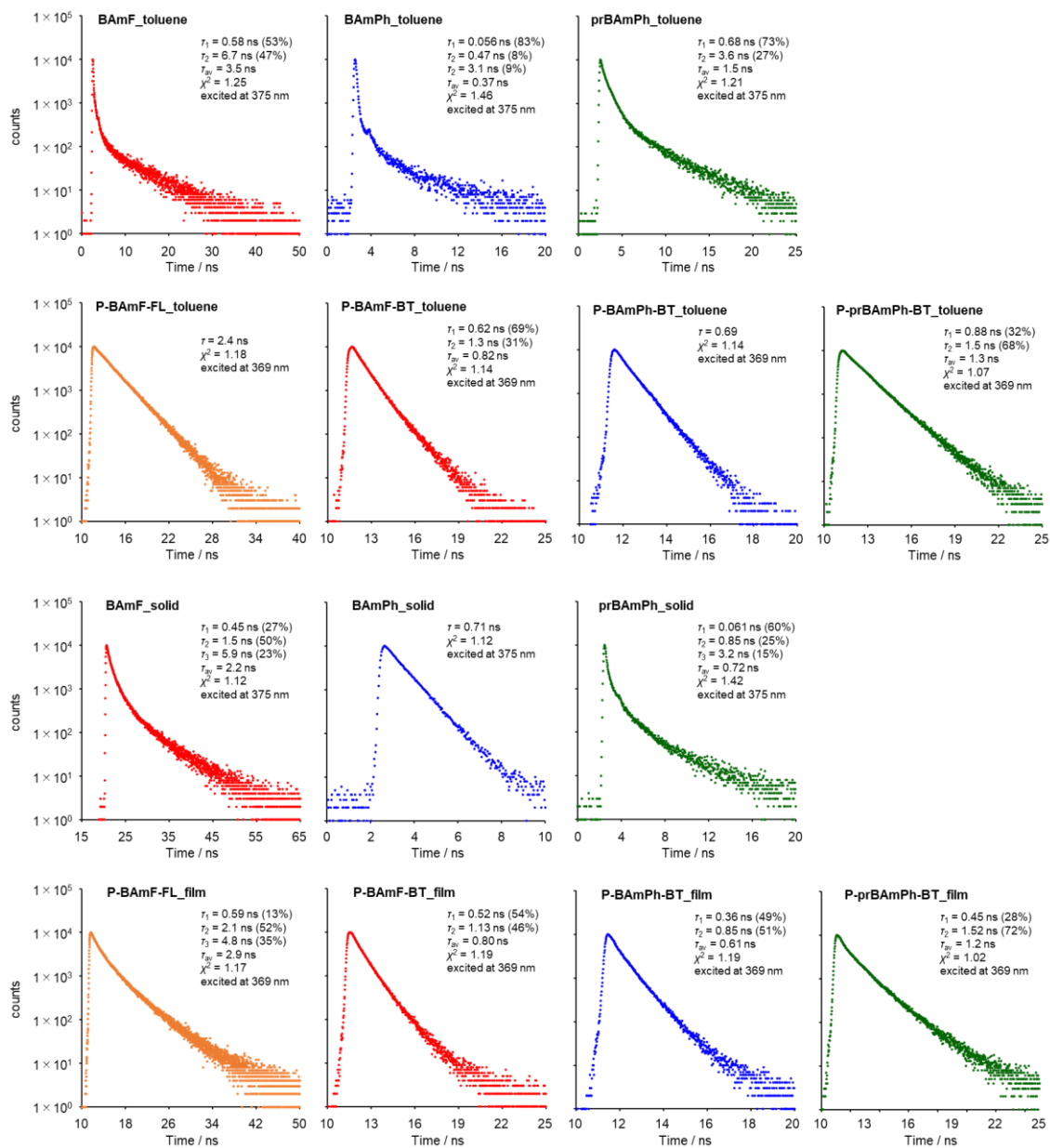


Figure S2. PL lifetime decay curves of BAM derivatives in toluene/CHCl₃ = 99/1 v/v (1.0×10⁻⁵ M) at room temperature, excited by 375 nm LED laser. Their emissions at the PL peak tops were monitored.

Cyclic voltammograms

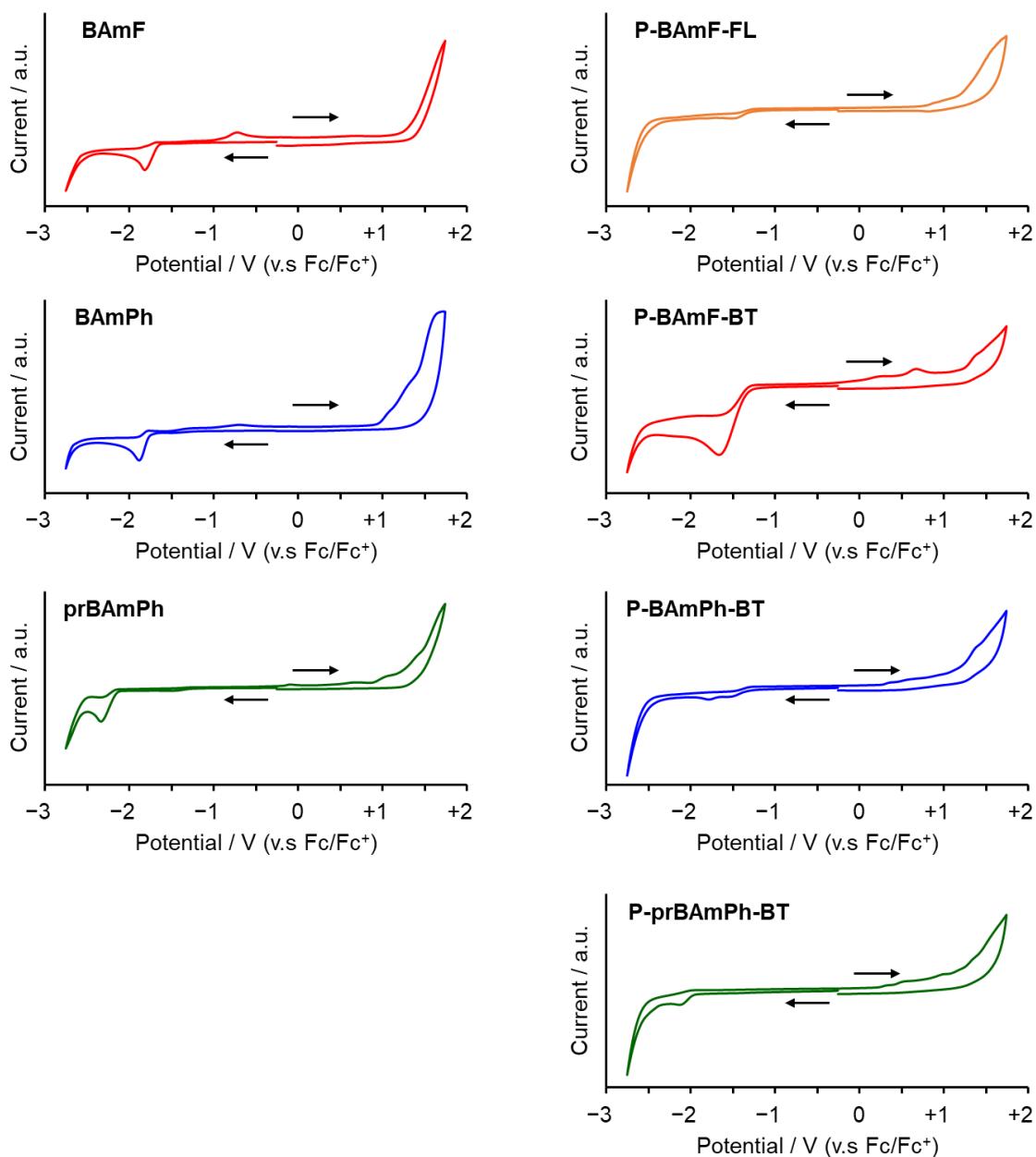


Figure S3. Cyclic voltammograms of BAM derivatives in CH₂Cl₂ (1.0×10^{-3} M) with a grassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc⁺) external reference at a scan rate of 0.1 V s^{-1} . The black arrows denote sweep directions (negative scan).

Computational details for theoretical calculation

The Gaussian 16 program package⁵ was used for computation. We optimized the structures of the **BAmF**, **BAmPh**, **prBAmPh**, **M-BAmF-FL (O_M-FL)**, **M-BAmF-BT (O_M-BT)**, **M-BAmPh-BT**, **M-prBAmPh-BT**, **P_M-FL**, **P_M-BT**, **M3-BAmF-FL (O_M3-FL)**, **M3-BAmF-BT (O_M3-BT)**, **M3-BAmPh-BT**, **M3-prBAmPh-BT**, **P_M3-FL**, and **P_M3-BT** in the ground S_0 states and calculated their molecular orbitals (Figure S4). Long alkyl chains were converted to methyl groups to save the calculation cost. The density functional theory (DFT) was applied for the optimization of the structures in the S_0 states at B3LYP/6-311G(d,p) level. We calculated the transition energy with optimized geometries in the S_0 states by time-dependent (TD) DFT at B3LYP/6-311G(d,p) level.

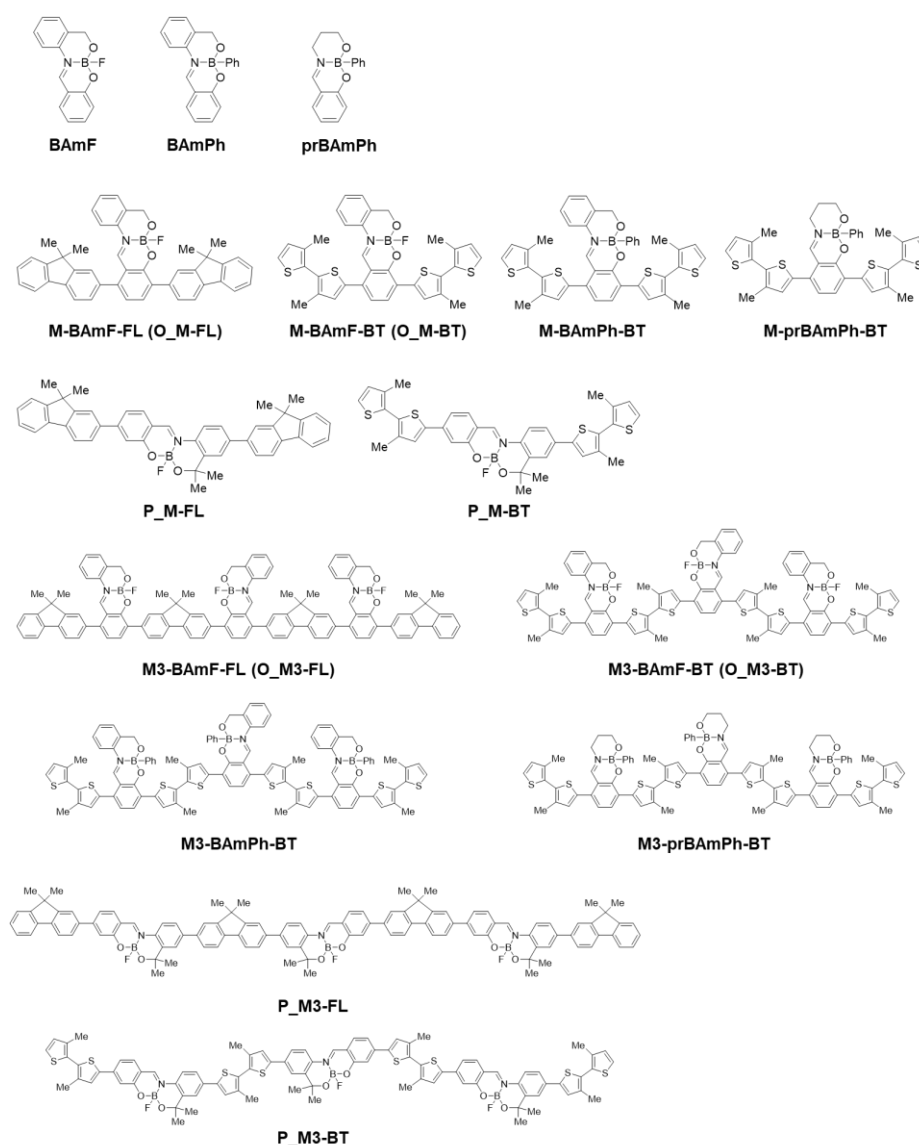


Figure S4. Chemical structures of BAm derivatives for theoretical calculation.

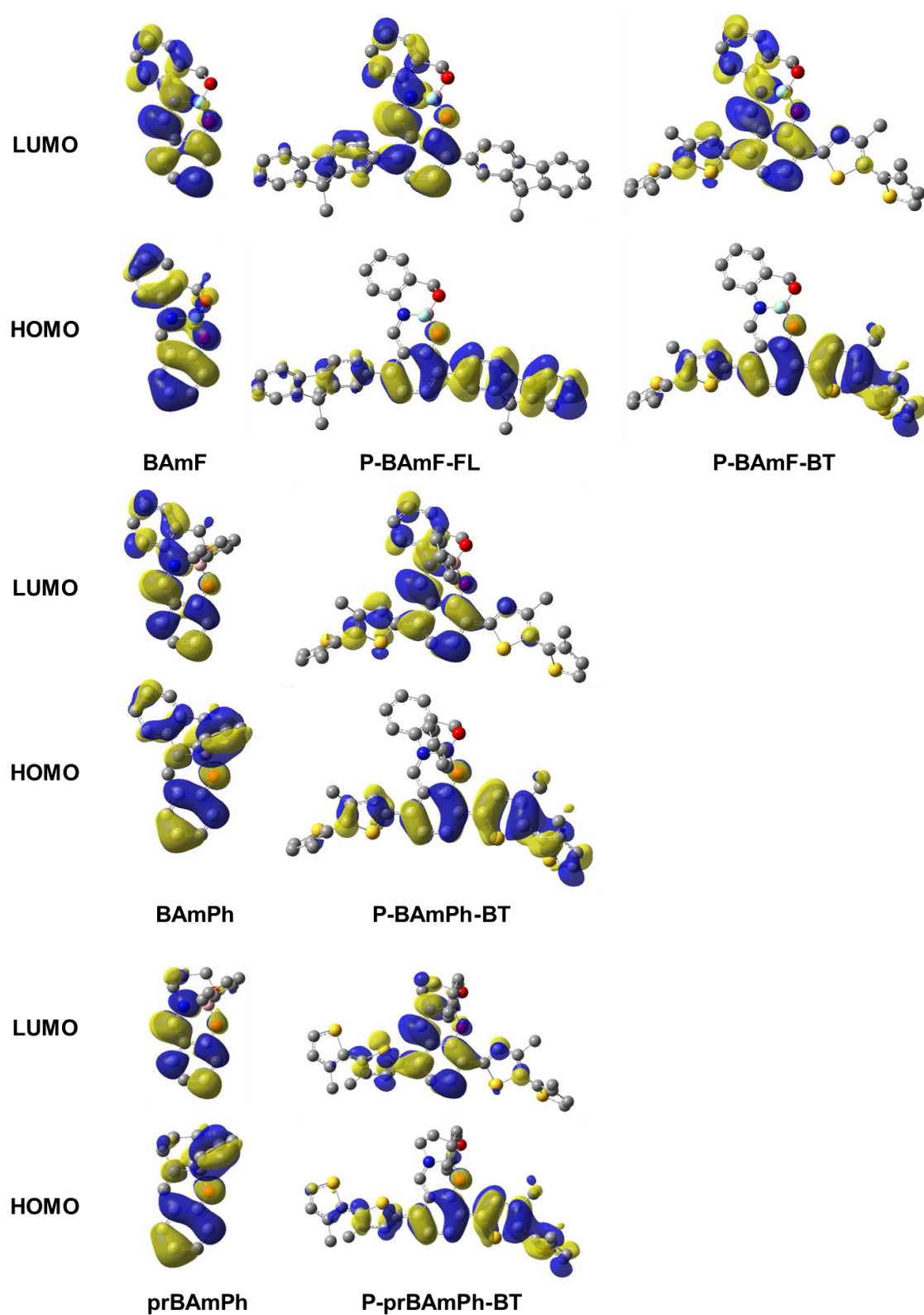


Figure S5. Selected Kohn–Sham orbitals of BAM derivatives obtained with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

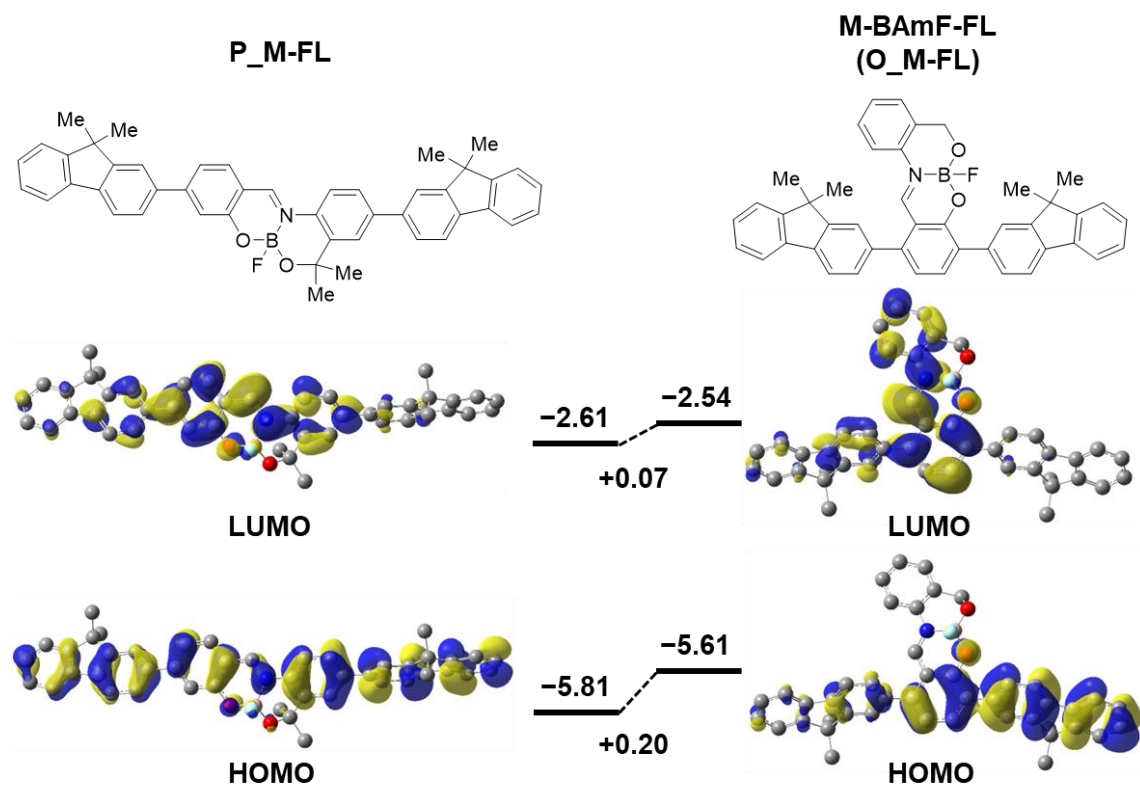


Figure S6. Chemical structures, energy diagrams, and Kohn-Sham orbitals of model compounds of polymers with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

Thermal stability test

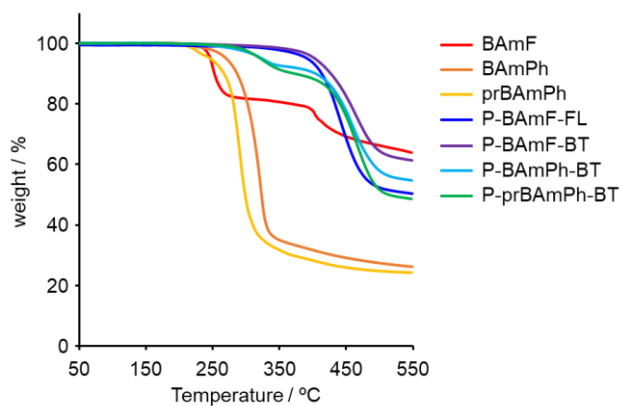


Figure S8. TGA curves of powder samples of BAm derivatives under N₂ (scan rate, 10 °C min⁻¹).

Table S2. Decomposition temperatures of BAm derivatives

	T_{d1}^a	T_{d2}^b
	/°C	/°C
BAmF	242	396
BAmPh	296	—
prBAmPh	275	—
P-BAmF-FL	406	—
P-BAmF-BT	414	
P-BAmPh-BT	288	426
P-prBAmPh-BT	293	432

^a Onset temperature of the first degradation curve calculated from an extrapolation method

^b Onset temperature of the second degradation curve calculated from an extrapolation method

Photostability test

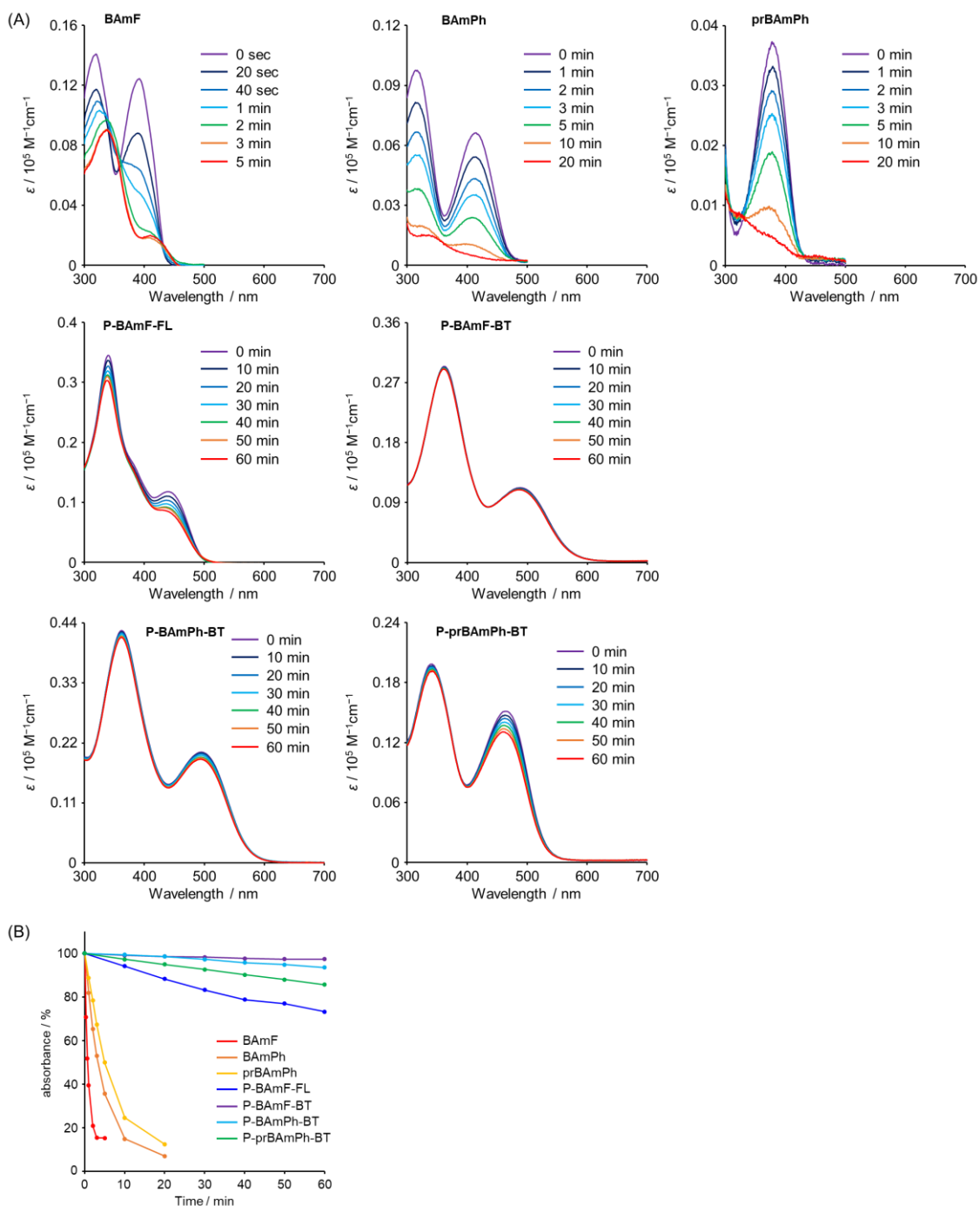


Figure S9. (A) Photostability tests of BAm derivatives in toluene ($1.0 \times 10^{-5} \text{ M}$ for monomeric units, $1.0 \times 10^{-5} \text{ M}$ per repeating units for polymers) irradiated by transilluminator (365 nm). (B) Summary of time-dependent absorbance monitored at the longest absorption band.

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