

Side-Chain Engineering of Boron β -Dialdiminate Homopolymer for Solvent-Dependent Emission Properties

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Abstract

Luminescent materials that respond to changes in microscopic chemical conditions are essential for visualizing and evaluating molecular environments. Boron complexes are often employed as robust scaffolds for constructing such responsive systems because of their inherent stimuli-responsive properties. However, in the case of nonresponsive luminophores, the absence of these intrinsic features limits their range of applications. In this study, we developed environment-responsive luminescent homopolymers based on the boron β -dialdiminate complex, which is intrinsically less responsive, by introducing optimized side chains. As a key finding, the triethylene glycol-decorated polymer exhibits more intense luminescence in chloroform but weaker luminescence in *N,N*-dimethylformamide. Structural analyses using NMR and size-exclusion chromatography suggest that this polymer forms larger aggregates in polar solvents because of the solvophobicity of its main chain, while the polar side chains assist to maintain adequate dispersibility of these aggregates. Photophysical measurements indicate that interchromophore interactions within the aggregates should be responsible for the reduced luminescence in polar solvents. These findings suggest that side-chain engineering should be an effective strategy for creating stimuli-responsive polymers from otherwise nonresponsive luminophores.

Introduction

Organic sensors with π -conjugated compounds are applicable for detecting small changes in external environments.^[1] Particularly, luminescent materials have contributed to the enhancement of sensitivity because of their drastic changes in their photophysical properties.^[2] Boron-containing luminophores are advantageous scaffolds for constructing fluorescence sensors because of their efficient luminescent properties, tunable luminescent properties from fluorescence to phosphorescence, and highly sensitive responsiveness toward environmental changes.^[3] From previous research, variety of fluorescence sensors consisting of the conjugated polymers based on boron complexes have been developed for obtaining effective detection systems by utilizing the interactions between directly attached repeating units,^[4] and intra- and interchain interactions.^[5,6] For most of these examples, their stimuli responsiveness originates mainly from their monomer units, which are intrinsically responsive to environmental changes. Nevertheless, π -conjugated polymeric structures could potentially contribute to enhancing the sensitivity.^[7] Therefore, the utilization of polymeric structures has still encouraged us to develop sensing materials.

Recently, stimuli-responsive polymers based on various boron complexes have been achieved, for instance, ketoiminate,^[6,8] azomethine,^[9] and β -diketiminato complexes.^[5] We have also reported the π -conjugated polymers composed of β -dialdiminato (DAI) boron complexes with various comonomers showed efficient luminescence in both solution and solid states because of the absence of rapid nonradiative quenching paths.^[10] Therefore, it could be hypothesized that high-contrast stimuli-responsive luminescent materials could be achieved by using DAI complexes. However, the stimuli responsiveness of these polymers was hardly observed because their interchromophore interactions were not significantly changed by external stimuli. Hence, we presumed that switchable interchromophore interactions might facilitate stimuli responsiveness of the DAI-based systems. One of possible methods for achieving the switchable interactions from DAI polymers is to modify their morphology in solutions with side-chain engineering. The morphology of polymers depends strongly on the solvophobic effect, which is responsible for foldamers.^[11] For instance, Koeckelberghs. *et al.* reported that polythiophene with specific side chains adopted a helical structure and showed the different light-absorption property in poor solvents.^[12] Herein, we show three DAI homopolymers, which have different alkyl ether and oligoether groups as the side chains. Comparison of photophysical properties among the synthesized polymers in solution states clarified that the polymers exhibit solvent-dependent emission in specific conditions. Spectroscopic and structural analyses implied that the solvophobic effect could lead to those environment-responsive luminescence.

Results and Discussion

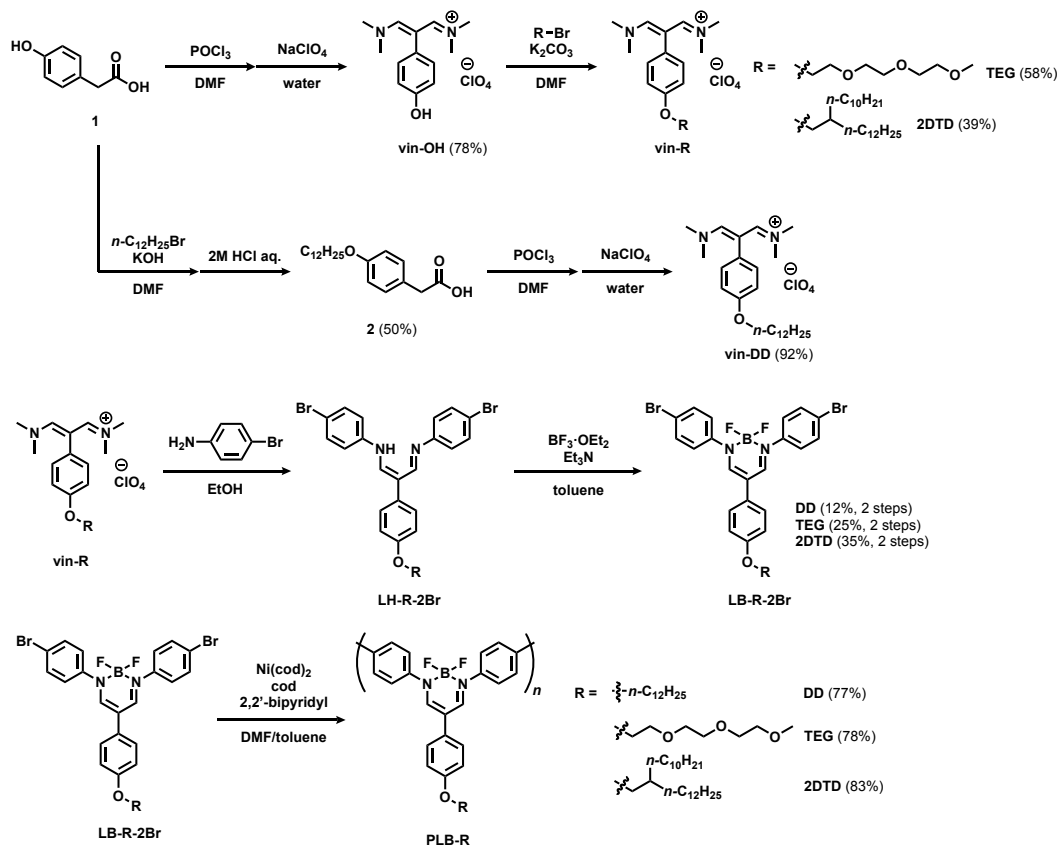
Synthesis

Boron DAI homopolymers were synthesized according to Scheme 1. The vinamidinium salt **vin-**

OH, which has a hydroxyl group on the *para* position of its phenyl group, was synthesized from 4-hydroxyphenylacetic acid through the modified procedure of the literature.^[13] **vin-TEG** and **vin-2DTD** were obtained through the Williamson ether synthesis of **vin-OH** with **TEG-Br** and 11-(bromomethyl)tricosane **2DTD-Br**, respectively. On the other hand, the dodecyl-substituted derivative **vin-DD** was synthesized according to the previous research.^[14] The condensation of these vinamidinium salts and 4-bromoaniline gave the dialdimine ligands **LH-R-2Br** (R = DD, TEG, and 2DTD). The reaction of **LH-R-2Br** and trifluoroborane diethyl etherate afforded the DAI monomers **LB-R-2Br** (R = DD, TEG, and 2DTD). The desired homopolymers **PLB-R** were synthesized through the Yamamoto coupling reaction with **LB-R-2Br**. The polymer properties, such as number-average molecular weight (M_n), weight-average molecular weight (M_w), molecular weight distribution (M_w/M_n) and number-average degree of polymerization (DP), were estimated by size-exclusion chromatography (SEC) in chloroform as an eluent with the polystyrene standards (Table 1). As the comparison with these polymers, the corresponding model compounds, which have the same side chains, were also prepared as shown in Scheme 1. Their chemical structures were confirmed by ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy and HRMS. MALDI-TOF-MS analysis suggested that the terminal groups of all homopolymers were mainly hydrogen atoms.

Scheme 1. Synthetic scheme of DAI polymers **PLB-R** and model compounds **LB-R** (cod: cycloocta-1,5-diene)

Polymers



Model compounds

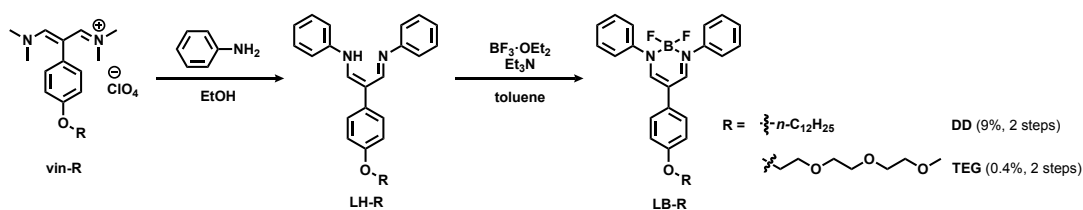


Table 1. Results of polymerization of DAI homopolymers^a

	M_n	M_w	M_w / M_n	DP^b
PLB-DD	53,000	130,000	2.5	100
PLB-TEG	13,000	29,000	2.2	26
PLB-2DTD	42,000	130,000	3.2	61

^a Estimated by SEC with the polystyrene standards in CHCl₃. ^b Average number of repeating units calculated from M_n and molecular weights of the repeating units.

Photophysical Properties of Model Compounds

The photophysical properties of model compounds **LB-DD** and **LB-TEG** were investigated (Figure 1 and Table 2). Initially, UV-vis absorption and photoluminescence (PL) spectra of **LB-R** in chloroform solutions (1.0×10^{-5} M) were measured for clarifying their electronic structures without significant interchromophore interactions. The spectra of monomeric complex **Ph_LB**^[10] (Figure 1a) are also shown as the comparison. All samples showed strong absorption and emission bands in the visible region attributable to the π - π^* transition. The optical bands of **LB-DD** and **LB-TEG** were bathochromically shifted compared to those of **Ph_LB**, probably because of the electron-donating nature of the -OR group. In addition, an absolute photoluminescence quantum yield (PLQY, Φ_{PL}) was enhanced by the introduction of the alkoxy group compared to **Ph_LB**. Photoluminescence lifetime (τ) measurement revealed that the PLQY enhancement should originate from the smaller nonradiative deactivation rate constant (k_{nr}) rather than the change in radiative one (k_{r}). Importantly, no significant difference in electronic properties between **LB-R** with different side chains was observed.

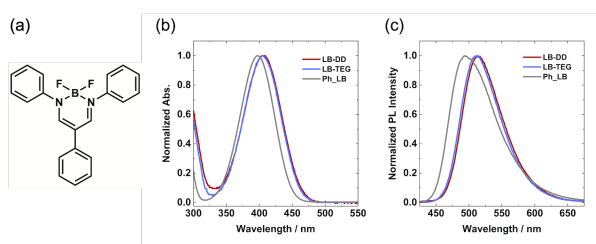


Figure 1. (a) Chemical structure of **Ph_LB**. (b) Normalized UV-vis absorption and (c) PL spectra in chloroform solutions (1.0×10^{-5} M) of **LB-DD**, **LB-TEG** and **Ph_LB**.

Table 2. Photophysical properties of **LB-DD**, **LB-TEG**, and **Ph_LB** in solutions^a

LB-DD							
solvent	ε / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
hexane	1.6	407	507	0.70	3.2 (0.84%), 6.3 (99.16%)	1.1	0.48
toluene	1.6	411	510	0.71	6.0	1.2	0.48
chloroform	1.5	407	514	0.69	7.0	0.99	0.45
ethyl acetate	1.5	407	510	0.65	3.4 (1.15%), 6.8 (98.85%)	0.96	0.52
DMSO	1.4	413	526	0.72	0.42 (1.00%), 7.6 (98.84%)	0.96	0.38
ethanol	1.5	407	516	0.66	7.2	0.91	0.47
LB-TEG							
solvent	ε / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
hexane	1.3	406	504	0.69	6.2	1.1	0.50
toluene	1.4	410	510	0.71	3.5 (2.18%), 7.0 (97.82%)	1.0	0.41
chloroform	1.3	405	512	0.71	6.7	1.1	0.43
ethyl acetate	1.3	407	513	0.65	7.6	1.0	0.52
DMSO	1.3	411	525	0.73	7.4	1.0	0.36
ethanol	1.3	406	513	0.64	6.9	0.9	0.51
Ph_LB ^h							
solvent	ε / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
chloroform	1.6	398	495	0.48	3.0	1.6	1.7

^a Photophysical properties were recorded for 1.0×10^{-5} M solutions. ^b Molar absorption coefficient. ^c Wavelength at absorption maxima. ^d Wavelength at emission maxima. Excited at λ_{abs} . ^e Absolute quantum yield determined by the integration sphere method. Excited at λ_{abs} . ^f Fluorescence lifetime determined by time-correlated single-photon counting. Excited with an LED laser at 375 nm. Fraction of component i , f_i , is shown in the parentheses. ^g k_{r} and k_{nr} were calculated with the following formula: $k_{\text{r}} = \Phi_{\text{PL}} / \langle \tau \rangle$; $k_{\text{nr}} = (1 - \Phi_{\text{PL}}) / \langle \tau \rangle$, where $\langle \tau \rangle = \sum f_i \tau_i$. ^h Data were taken from ref. [10].

To obtain deeper insights into the origin of bathochromic shifts, we carried out density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G+(d,p) level of theory (Figure 2 and Table 3) using the Gaussian 16 Rev. C.01 program package.^[15] To save the calculation time, **LB-Me**, which has a methoxy group instead of the long chains of **LB-R**, was employed for the calculations. The smaller transition energies for both S_0 and S_1 geometries of **LB-Me** than those of **Ph_LB** were comparable to the experimentally observed bathochromic shifts of absorption and emission spectra. According to the consideration of Kohn–Sham frontier orbital distributions, it is suggested that the narrower energy gaps of **LB-Me** result mainly from its higher highest occupied molecular orbital (HOMO) level. The electron-donating alkoxy group destabilized the HOMO of the complex, while the energy levels of the lowest unoccupied molecular orbital (LUMO) showed slight changes. This striking difference between the HOMO and LUMO should be derived from the nodal plane in the LUMO passing through the center of the molecule. Therefore, the orbital attributed to the methoxy group did not provide any significant contributions to the LUMO.

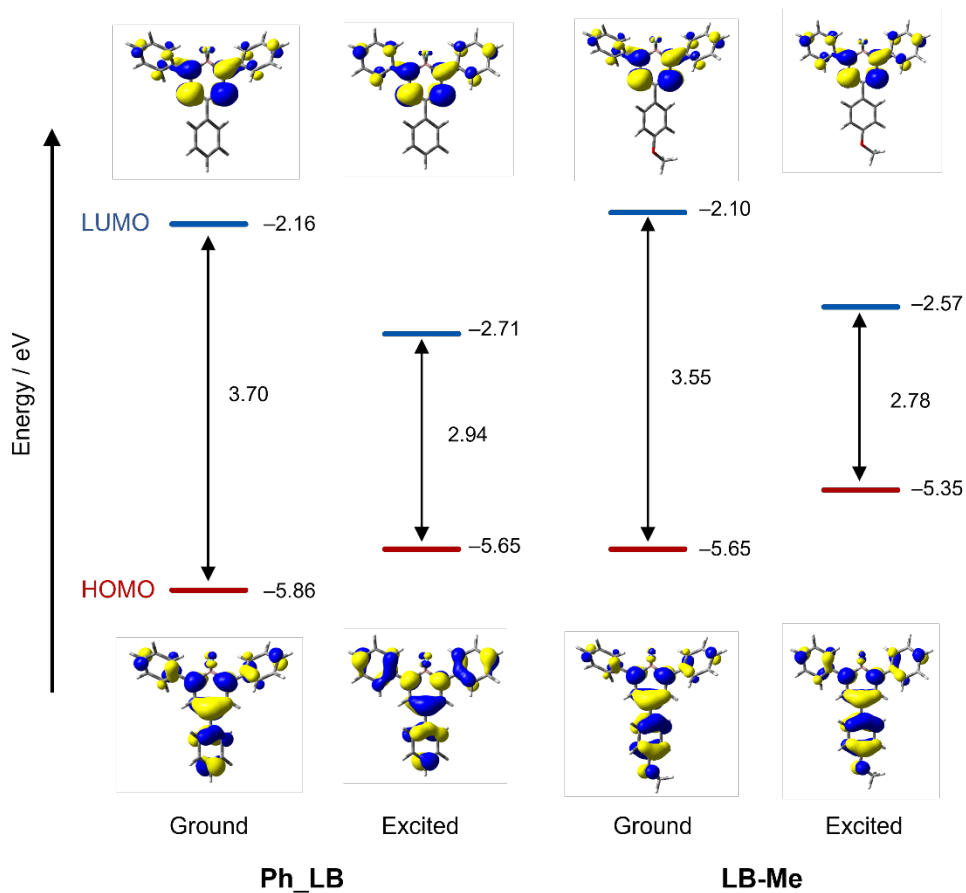


Figure 2. Structures and molecular orbital diagrams of the LUMOs and HOMOs of **Ph_LB** and **LB-Me** in the ground states obtained from the DFT calculations (B3LYP/6-31G+(d,p)//B3LYP/6-31G+(d,p)).

Table 3. Calculated parameters of S_1 states for optimized geometries in the ground (S_0) and excited states (S_1)

	Geometry	Composition	Coefficient	E / eV	λ / nm	f
Ph_LB	S_0	H→L	0.70434	3.34	372	0.3872
	S_1	H→L	0.70841	2.63	472	0.3972
LB-Me	S_0	H→L	0.70346	3.18	390	0.2734
	S_1	H→L	-0.70723	2.49	499	0.2375

In order to investigate the effects of solvents on photophysical properties, we next measured photophysical properties of **LB-R** in hexane, toluene, chloroform, ethyl acetate, dimethyl sulfoxide (DMSO), and ethanol (1.0×10^{-5} M, solvent/ CHCl_3 = 99/1, v/v) (Figure 3 and Table 2). It was revealed that **LB-R** kept efficient emission in all solvents. The emission wavelengths shifted to the slightly longer wavelength region in polar solvents. The Lippert–Mataga plots were prepared from the values of Stokes shift in each solvent and the Lippert's polarity parameter Δf (Figure 3c and g).^[16,17] The positive slopes indicated that the intramolecular charge transfer (ICT) properties of the S_1 state of these compounds should lead to the bathochromic shifts of the spectra in the polar media.

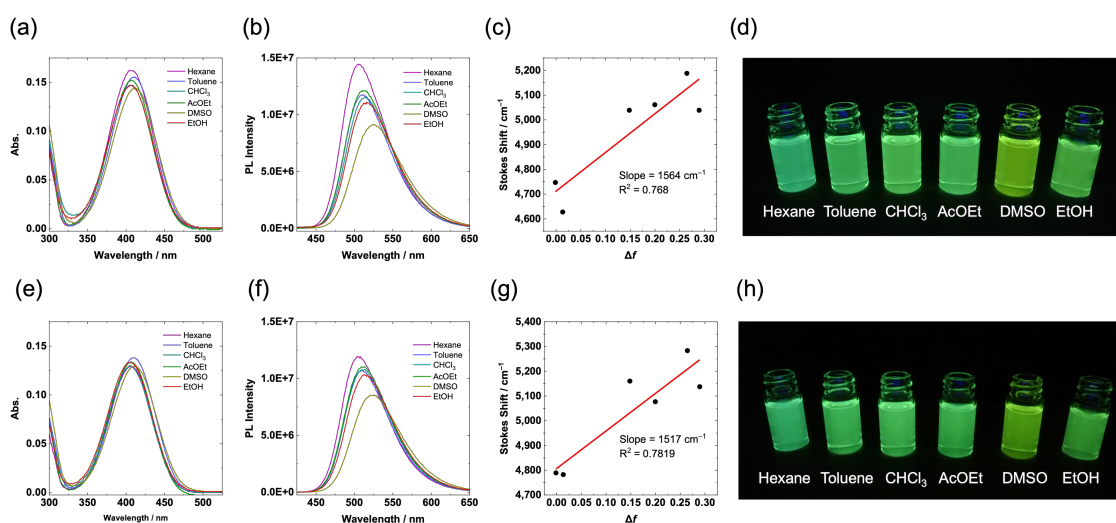


Figure 3. (a,e) UV–vis absorption and (b,f) PL spectra in various solutions (1.0×10^{-5} M) and (c,g) Lippert–Mataga plot of **LB-DD** and **LB-TEG**, respectively. Photographs of (d) **LB-DD** and (h) **LB-TEG** in various solutions (1.0×10^{-5} M) under UV irradiation (365 nm).

Photophysical Properties of PLB-R

Photophysical properties of **PLB-R** in solutions were measured and compared to those of the model compounds (Figure 4 and Table 4). In chloroform solutions (1.0×10^{-5} M), all polymers exhibited efficient emission like **LB-R**. Meanwhile, apparent bathochromic shifts in both absorption and PL spectra were observed compared to those of **LB-R**, indicating the extension of π -conjugation. Importantly, the types of the side chains lead to no significant changes in the absorption and emission properties under this condition.

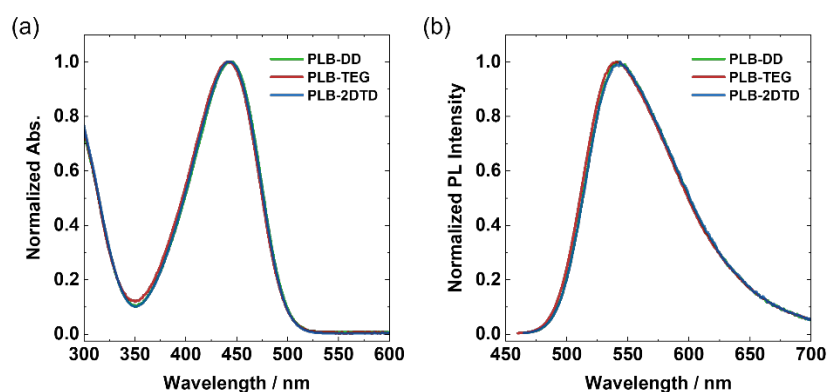


Figure 4. (a) Normalized UV-vis absorption and (b) PL spectra in chloroform solutions (1.0×10^{-5} M) of **PLB-R**.

Table 4. Photophysical properties of **LB-DD**, **LB-TEG** and **LB-2DTD** in chloroform solutions^a

	ε / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
PLB-DD	2.4	445	542	0.79	0.38 (1.58%) 3.0 (98.42%)	2.7	0.71
PLB-TEG	2.4	442	541	0.60	1.1 (9.29%) 2.8 (90.71%)	2.3	1.5
PLB-2DTD	2.6	444	544	0.76	2.6 (73.15%) 4.1 (26.85%)	2.6	0.79

^a Photophysical properties were recorded for 1.0×10^{-5} M solutions. ^b Molar absorption coefficient. ^c Wavelength at absorption maxima. ^d Wavelength at emission maxima. Excited at λ_{abs} . ^e Absolute quantum yield determined by an integration sphere method. Excited at λ_{abs} . ^f Fluorescence lifetime determined by time-correlated single-photon counting. Excited with an LED laser at 375 nm. Fraction of component i , f_i , is shown in the parentheses. ^g k_{r} and k_{nr} were calculated with the following formula: $k_{\text{r}} = \Phi_{\text{PL}} / \langle \tau \rangle$; $k_{\text{nr}} = (1 - \Phi_{\text{PL}}) / \langle \tau \rangle$, where $\langle \tau \rangle = \sum f_i \tau_i$.

DFT calculations at the B3LYP/6-31G+(d,p) level of theory were carried out with a model dimer **2LB-Me**, which has methoxy groups in the place of the side chain (Figure 5 and Table 5). The relatively small transition energies of **2LB-Me** were consistent with the red-shifted absorption and PL spectra of **PLB-R** compared to the small molecules. The HOMO level of **2LB-Me** was higher than that of **LB-Me**, while its LUMO level was lower. Therefore, it was suggested that the narrower energy gaps resulted from the extension of π -conjugation in both LUMO and HOMO. It is worth noting that the HOMO and LUMO distributions of the original complex was preserved in each complex moiety in the dimer.

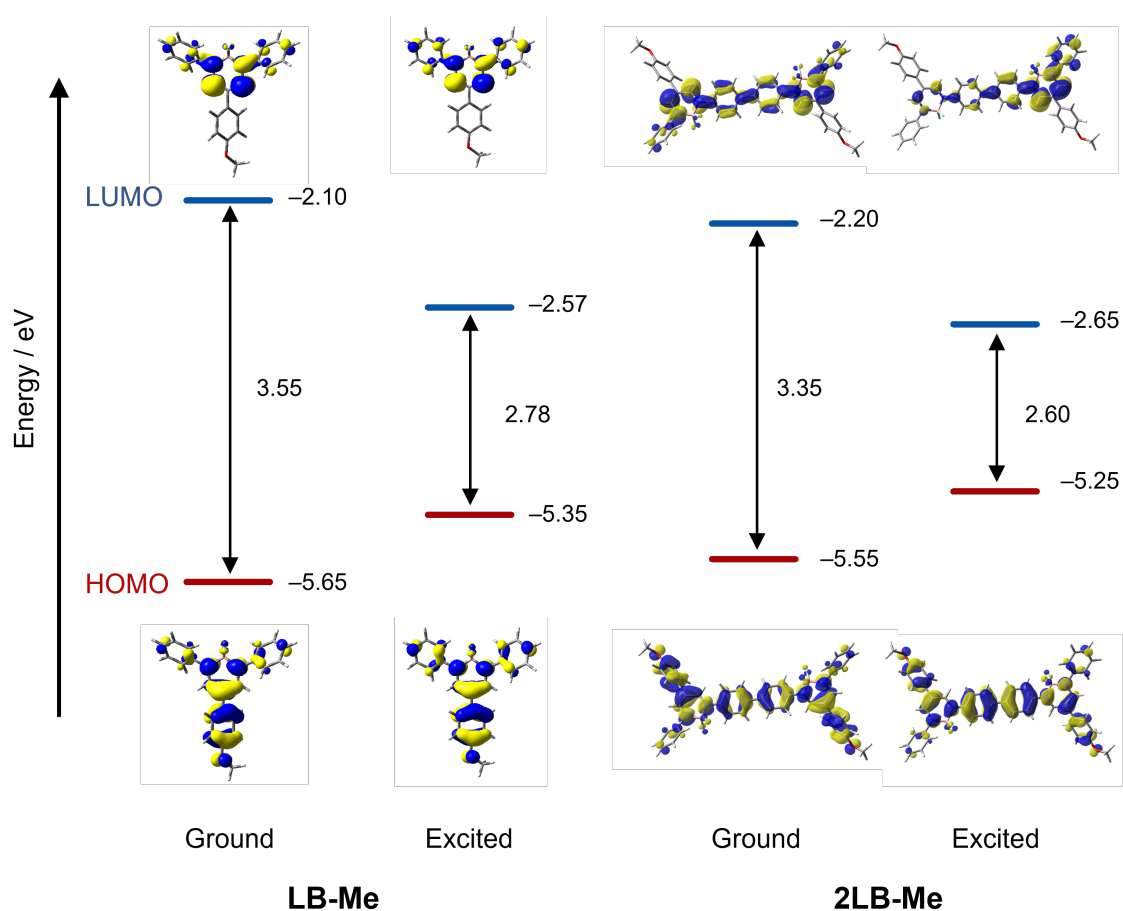


Figure 5. Structures and molecular orbital diagrams of the LUMOs and HOMOs of **LB-Me** and **2LB-Me** in the ground states obtained from the DFT calculations (B3LYP/6-31G+(d,p)//B3LYP/6-31G+(d,p)).

Table 5. Calculated parameters of S_1 states for optimized geometries in the ground (S_0) and excited states (S_1)

Sample	Geometry	Composition	Coefficient	E / eV	λ / nm	f
LB-Me	S_0	H $\rightarrow$ L	0.70346	3.18	390	0.2734
	S_1	H $\rightarrow$ L	-0.70723	2.49	499	0.2375
2LB-Me	S_0	H $\rightarrow$ L	0.67869	2.95	420	0.9397
		H-1 $\rightarrow$ L+1	-0.18243			
	S_1	H $\rightarrow$ L	-0.69798	2.29	542	1.0983

Solvent-Dependent Emission Properties of PLB-R

The photophysical properties of the **PLB-TEG** and **PLB-2DTD** were measured in hexane, chloroform, *N,N*-dimethylformamide (DMF), and DMSO (1.0×10^{-5} M, solvent/ $\text{CHCl}_3 = 99/1$, v/v) (Figure 6 and Table 6). Most importantly, it was demonstrated that the emission of **PLB-TEG** in DMSO and DMF was dramatically quenched with the bathochromic shifts of absorption and emission wavelengths, compared to those in chloroform. **PLB-2DTD** showed similar but relatively small changes in photophysical properties in hexane. These changes of emission properties were less drastically observed in the model compounds **LB-R** (Figure 3 and Table 2). These data indicate that solvent-dependent emission properties of DAI-based polymers can be modulated by side-chain engineering of homopolymers. It should be mentioned that **PLB-DD** showed relatively low solubility in DMSO, DMF, and hexane. In addition, **PLB-TEG** was insoluble in hexane, while **PLB-2DTD** was not well soluble in DMSO and DMF. Chloroform was a good solvent for all the polymers. This solubility difference suggests that the polymer mainchain should not be efficiently solvated in both polar (DMF and DMSO) and less polar (hexane) solvents. On the other hand, the polar TEG and the aliphatic 2DTD side chains could afford the dispersibility of the corresponding polymers in the polar and less polar solvents, respectively.

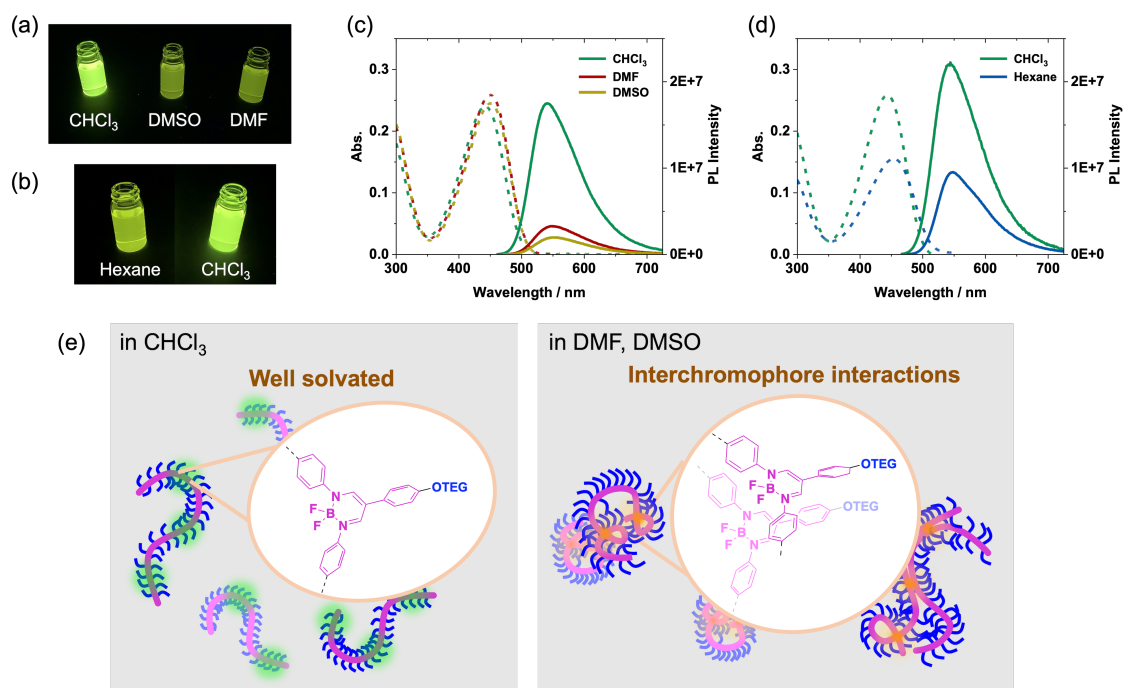


Figure 6. Photographs of (a) **PLB-TEG** and (b) **PLB-2DTD** in various solutions (1.0×10^{-5} M) under UV irradiation (365 nm). UV-vis absorption and PL spectra in various solutions (1.0×10^{-5} M) of (c) **PLB-TEG** and (d) **PLB-2DTD**. (e) Schematic illustration of the plausible mechanism of the solvent-dependent emission behavior of **PLB-TEG**.

Table 6. Photophysical properties of **PLB-TEG** and **PLB-2DTD** in various solvents

PLB-TEG							
Solvent	ϵ / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
CHCl ₃	2.4	442	541	0.60	1.1 (9.29%) 2.8 (90.71%)	2.3	1.5
DMF	2.6	451	549	0.12	0.34 (28.49%) 0.61 (71.51%)	2.2	16
DMSO	2.4	452	550	0.08	0.30 (72.50%) 0.48 (27.50%)	2.3	26
PLB-2DTD							
Solvent	ϵ / $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ^b	λ_{abs} / nm ^c	λ_{PL} / nm ^d	Φ_{PL} ^e	τ / ns ^f	k_{r} / 10^8 s^{-1} ^g	k_{nr} / 10^8 s^{-1} ^g
CHCl ₃	2.6	444	544	0.76	2.6 (73.15%) 4.1 (26.85%)	2.6	0.79
Hexane	1.6	455	548	0.64	1.5 (26.67%) 3.0 (73.33%)	2.5	1.4

^a Photophysical properties were recorded for 1.0×10^{-5} M solutions. ^b Molar absorption coefficient. ^c Wavelength at absorption maxima. ^d Wavelength at emission maxima. Excited at λ_{abs} . ^e Absolute quantum yield determined by an integration sphere method. Excited at λ_{abs} . ^f Fluorescence lifetime determined by time-correlated single-photon counting. Excited with an LED laser at 375 nm. Fraction of component i , f_i , is shown in the parentheses. ^g k_{r} and k_{nr} were calculated with the following formula: $k_{\text{r}} = \Phi_{\text{PL}} / \langle \tau \rangle$; $k_{\text{nr}} = (1 - \Phi_{\text{PL}}) / \langle \tau \rangle$, where $\langle \tau \rangle = \sum f_i \tau_i$.

In order to investigate origins of the changes in PLQY, we compared their rate constants in various solvents (Table 6). The k_{nr} values of **PLB-TEG** in DMF and DMSO were ten times larger than that in chloroform, while the k_r values were almost identical. For **PLB-2DTD**, k_{nr} in hexane was twice larger than in chloroform, although k_r was hardly affected. Therefore, the smaller Φ_{PL} in specific solvents should be derived mainly from the acceleration of nonradiative decay processes. Moreover, since the PL lifetimes of **PLB-R** in the solid states were shorter than those in the solution states, the emissive species of **PLB-TEG** in the polar solvents and of **PLB-2DTD** in hexane were similar to those in the solid states (Figure S1 and Table S1). It is assumed that interchromophore interactions could lead to the larger k_{nr} with the little change in k_r . Overall, it is suggested that the solvent-dependent emission properties stem from the interchromophore interactions of the DAI units in the specific solvents.

To obtain deeper insights into the microscopic structure of the polymers in the different solvents, we estimated the hydrodynamic radius of **PLB-TEG** with SEC and diffusion-ordered NMR spectroscopy (DOSY). From the SEC chart of **PLB-TEG** in CHCl₃ and DMF (Figure S2 and Table 7), relative molecular weight was larger in DMF ($M_n = 16,000$) than that in CHCl₃ ($M_n = 13,000$). In addition, hydrodynamic radius (R_H) of the polymer was evaluated by DOSY with the Stokes–Einstein equation (Eq. 1):

$$D = \frac{k_B T}{6\pi\eta R_H} \quad (\text{Eq. 1})$$

where D is the diffusion coefficient that is obtained with DOSY NMR spectra, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solution. As shown in Table 8, all polymers in CDCl₃ have similar R_H (1.0–1.6 nm), resulting from the similar diffusion coefficients ($\sim 3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$). In contrast, the R_H value of **PLB-TEG** in DMF-*d*₇ was five times larger than that in CDCl₃, implying the formation of larger structures probably consisting of more than a single polymer chain. The decrease in PLQY in DMF and DMSO solutions could originate from the interchromophore interactions in those structures. The difference in solvation types between the DAI main chains and the side chains should cause the dramatic structural changes of the polymer chains.

Table 7. Results of SEC of **PLB-TEG**

Solvent	M_n	M_w	M_w/M_n	DP^b
CHCl ₃	13,000	29,000	2.2	26
DMF	16,000	56,000	3.6	31

Table 8. Results of DOSY NMR spectroscopy for **PLB-R**

Sample	Solvent	$D / \text{m}^2 \text{s}^{-1}$	$\eta / \text{g m}^{-1} \text{s}^{-1}$	T / K	R_H / nm
PLB-TEG	CDCl ₃	4.4×10^{-10}	0.51	303	1.0
	DMF- <i>d</i> ₇	5.8×10^{-11}	0.79	303	5.2
PLB-DD	CDCl ₃	3.7×10^{-10}	0.51	303	1.2
PLB-2DTD	CDCl ₃	2.7×10^{-10}	0.51	303	1.6

Finally, the plausible mechanism of the solvent-dependent emission for **PLB-TEG** is illustrated in Figure 6e as a representative example. In the chloroform solution, the polymer chains are solvated well because chloroform should be a good solvent for both main and side chains. The relatively weak interchromophore interactions in the excited state result in the efficient emission from a single chromophore. On the other hand, in the polar solvents like DMF and DMSO, the larger aggregates might be formed because of the solvophobic behavior of the main chains, while the side chains should enable the aggregates to disperse macroscopically. These aggregated but homogeneously dispersed structures could provide the smaller Φ_{PL} derived from the acceleration of nonradiative decay processes stemming from the stronger interchromophore interactions. Indeed, conventional conjugated polymers, like poly(phenylene vinylene), often exhibit solvent-dependent optical properties resulting from the formation of aggregates.^[18,19] For **PLB-2DTD**, the aliphatic side chains could afford the aggregates dispersibility in the less polar solution like hexane. Therefore, the decline in PLQY was observed from the hexane solution. Only minor changes were observed in this case, probably because the branched alkyl chains should be too bulky to adapt to strong interchromophore interactions. In other words, the lower steric hindrance of the oligo(ethylene glycol) chain of **PLB-TEG** could result in the more drastic change in the photoluminescence efficiency.^[20] It was demonstrated that the polarity and steric hinderance of the side chains could have the potential to tune the responsiveness of luminescent polymers to solvent polarity.

Conclusion

We synthesized the DAI homopolymers decorated by side chains with different polarities. **PLB-TEG** and **PLB-2DTD** showed solvent-dependent emission properties. Their emission bands were weakened in the specific solvents which are solvated only their side chains. The results of SEC and DOSY NMR demonstrated that the formation of aggregates in these solvents should lead to the emission annihilation through interchromophore interactions. Our findings could be applicable for developing stimuli-responsive materials utilizing the efficient emission of DAI both in solutions and solids.

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Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Side-Chain Engineering of Boron β -Dialdiminate Homopolymer for Solvent-Dependent Emission Properties

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Experimental Section

1. Measurements

^1H (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100 MHz), and $^{11}\text{B}\{^1\text{H}\}$ (128 MHz) NMR spectra were recorded on a JEOL JNM-AL400 spectrometer and a JEOL JNM-ECA600P spectrometer. ^1H DOSY NMR spectra were recorded on a JEOL JNM-ECA600P spectrometer. In ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, tetramethylsilane (TMS) and/or residual solvent peaks were used as an internal standard, and ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{OEt}_2$ (sealed capillary). 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 Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and a Bruker Daltonics ultrafleXtreme for matrix-assisted laser desorption ionization (MALDI). UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer and a SHIMADZU UV-3600i plus spectrophotometers. Gel permeation chromatography (GPC) was carried out on a TOSOH G3000HXL system and a SHIMADZU Prominence system equipped with three consecutive polystyrene gel columns (TOSOH gels: α -4000, α -3000, α -2500) using chloroform and DMF as eluents after calibration with standard polystyrene samples. Monomer fraction was carried out on a Recycling Preparative HPLC (LaboACE, Japan Analytical Industry Co., Ltd.). Fluorescence and phosphorescence emission spectra and phosphorescence decay were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics Quantaaurus-QY Plus C13534-01. Photoluminescence (PL) lifetimes were measured by a

Horiba FluoroCube spectrofluorometer system and excitation was carried out at 375 nm using a UV diode laser (NanoLED 375 nm). Dynamic light scattering was performed by Otsuka PRAR-1000.

2. Materials

Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-200 SiO₂. 4-Methoxyphenylacetic acid (Tokyo Chemical Industry Co, Ltd.; TCI), 4-hydroxyphenylacetic acid (TCI), 1-bromododecane (Wako), (TCI), 11-(bromomethyl)tricosane (TCI), aniline (Fujifilm Wako Pure Chemical Corporation; Wako), 4-bromoaniline (TCI), 4-iodoaniline (TCI), Ni(COD)₂ (TCI), 2,2'-bipyridyl (TCI), 1,5-cyclooctadiene (Wako), POCl₃ (TCI), NaClO₄ (Wako), K₂CO₃ (Wako), KOH (Wako), hydrochloric acid (Wako), BF₃•OEt₂ (Sigma-Aldrich Co., LLC.), anhydrous Na₂SO₄ (Wako), and anhydrous MgSO₄ (Wako) were purchased from the commercial sources and used as received. All solvents were purchased from Wako and used as received unless otherwise noted. Water was purified by Merck Millipore Automatic Sanitization Module. Diethyl ether (Wako) and triethylamine (Kanto Chemical Co., Inc.) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). **Ph_LB**,¹ **vin-OH**,² and **TEG-Br**³ were synthesized according to the literatures.

3. Synthetic Procedures and Characterizations

*3.1. Synthesis of **vin-OH***

vin-OH was synthesized according to a modified procedure of the literature.¹ To *N,N*-dimethylformamide (DMF, 13.0 mL) was added POCl₃ (9.30 mL, 15.3 g, 99.5 mmol) dropwise at room temperature under nitrogen. To the resulting reddish-brown solution was added a 4-hydroxyphenylacetic acid **1** (5.00 g, 32.9 mmol) and the mixture was stirred at 80 °C for 6 h. The reaction mixture was diluted with a small amount of DMF and added dropwise to NaClO₄ (4.46 g, 36.5 mmol) solution of EtOH (180 mL) and water (30 mL) at 0 °C. After cooling the solution in refrigerator for two days, all volatiles were removed with a rotary evaporator. The obtained mixture was added to water (300 mL) and stirred vigorously for 30 minutes at 0 °C. The precipitate was collected by filtration and washed with water and Et₂O, then dried in vacuum to afford the titled compound as pale white powder (8.2 g, 78%). ¹H NMR (DMSO-*d*₆): δ 9.75 (s, 1H), 7.64 (s, 2H), 7.06–7.02 (m, 2H), 6.81–6.77 (m, 2H), 3.21 (s, 6H), 2.47 (s, 6H) ppm. ¹³C{¹H} NMR (DMSO-*d*₆): δ 163.3, 157.6, 133.3, 122.2, 115.3, 105.3, 48.1, 39.0 ppm. HRMS (ESI) [M]⁺: Found, 219.1492; Calcd., 219.1497.

*3.2. General procedure for the synthesis of vinamidinium salts **vin-R** (R = **TEG**, **2DTD**)*

To a solution of **vin-OH** in DMF were added 1-bromoalkane **R-Br** (1.2 eq.), K₂CO₃ (2.5 eq.) at room temperature under nitrogen. The suspension was stirred at room temperature for 1 d. Purification methods were described in each section for the compounds.

3.2a. Synthesis of *vin-TEG*

vin-OH (6.00 g, 18.8 mmol), **TEG-Br** (5.13 g, 22.6 mmol), K₂CO₃ (6.50 g, 47.1 mmol), and DMF (19 mL) were employed. The reaction mixture was extracted with dichloromethane three times, then the organic layer was washed with brine and dried over anhydrous MgSO₄. The mixture was filtered, and all volatiles were removed with a rotary evaporator. The resulting oil was dried in vacuum. The brownish yellow oil was obtained as a mixture with the unidentified impurities (crude yield: 5.1 g, 58%). ¹H NMR (CDCl₃): δ 7.83 (s, 2H), 7.17–7.13 (m, 2H), 6.95–6.92 (m, 2H), 4.17–4.13 (m, 2H), 3.91–3.88 (m, 2H), 3.79–3.55 (br, 8H), 3.58–3.55 (m, 2H), 3.39 (s, 3H), 3.33 (s, 6H), 2.51 (s, 2H). ¹³C{¹H} NMR (CDCl₃): δ 164.3, 159.8, 133.8, 124.2, 115.03, 106.1, 72.2, 71.6, 71.0, 70.8, 69.9, 68.0, 49.3, 39.9. HRMS (ESI) [M+H]⁺: Found, 365.2431; Calcd. 365.2431, .

3.2b. Synthesis of *vin-2DTD*

vin-OH (1.50 g, 4.71 mmol), 11-(bromomethyl)tricosane **2DTD-Br** (2.35 g, 5.65 mmol), tetrabutylammonium iodide (70.2 mg, 0.19 mmol) K₂CO₃ (1.63 g, 11.8 mmol), and DMF (5.0 mL) were employed. The reaction mixture was neutralized with 1 M HCl aq. and extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous MgSO₄. The mixture was filtered, and all volatiles were removed with a rotary evaporator. The resulting mixture was purified by silica gel chromatography with ethyl acetate as an eluent. The obtained oil was dried in vacuum. The brownish yellow oil was obtained as a mixture with the compound containing one oxo enamine unit and unidentified impurities (crude yield: 1.2 g, 39%). ¹H NMR (CDCl₃): δ 9.07 (s, 1H), 7.08–7.05 (2H, m), 6.87–6.85 (2H, m), 6.78 (br, 1H), 3.82–8.80 (d, *J* = 5.4 Hz, 2H), 2.82 (s, 6H), 1.79–1.70 (m, 1H) 1.75–1.26 (br, 40H), 0.90–0.86 (t, 6H, *J* = 6.5

Hz.). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 190.0, 183.2, 158.4, 132.1, 131.8, 128.8, 114.1, 70.9, 44.1, 38.0, 35.3, 31.9, 31.4, 31.3, 31.3, 30.0, 29.7, 29.7, 29.6, 29.6, 29.3, 26.8, 26.1, 22.7, 14.1. HRMS (ESI) $[\text{M}+\text{H}]^+$: Found, 555.5241; Calcd., 555.5248.

3.3. Synthesis of **2**

Compound **2** was synthesized according to a modified procedure of the literature.⁴ To a solution of 4-hydroxyphenylacetic acid (20.0 g, 131 mmol), potassium hydroxide (14.8 g, 263 mmol) in ethanol (110 mL) was added 1-bromododecane (36.0 g, 34.7 mL, 145 mmol) under ambient condition. The mixture was stirred at reflux temperature for 14 h, and allowed to cool to 0 °C. After potassium hydroxide (7.38 g, 130 mmol) was added, the solution was refluxed for 2 h. The resulting solution was acidified with 2 M HCl aq. at 0 °C and extracted with cyclopentyl methyl ether (CPME) three times. The organic layer was washed with water and brine, then dried over anhydrous magnesium sulfate. The insoluble compounds were removed by filtration and the filtrate was concentrated with a rotary evaporator to give a white solid. The solid was washed with methanol to give a pure product as a white solid (21 g, 50%). Spectroscopic data of ¹H and ¹³C NMR were identical to the reported ones of the literature.⁴

3.4. Synthesis of **vin-DD**

To *N,N*-dimethylformamide (DMF, 4.3 mL) was added POCl₃ (3.1 mL, 32.8 mmol) dropwise at room temperature under nitrogen. To the resulting reddish-brown solution was added **2** (3.50 g, 10.9 mmol) and the mixture was stirred at 80 °C for 17 h. The reaction mixture was diluted with DMF and added dropwise to NaClO₄ (1.48 g, 12.1 mmol) aqueous solution at 0 °C. The precipitate was collected by suction filtration and washed with water and diethyl ether to give a product as a white powder (4.9 g, 92 %). ¹H NMR (CDCl₃): δ 7.87 (s, 2H), 7.14–7.11 (dd, 2H), 6.91–6.89 (dd, 2H), 3.98–3.94 (t, 2H, *J* = 6.6 Hz), 3.33 (s, 6H), 2.50 (s, 6H), 1.83–1.76 (quint. 2H), 1.48–1.27 (br, 18H), 0.90–0.86 (t, 3H, *J* = 6.8 Hz). ¹³C {¹H} NMR (CDCl₃): δ 164.3, 159.6, 133.1, 123.4, 114.6,

105.6, 68.1, 49.0, 39.5, 31.8, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 25.9, 22.5, 14.0. HRMS (ESI) $[M]^+$: Found, 387.3376; Calcd., 387.3370. Anal. Calcd. for $C_{25}H_{43}N_2O_5Cl$: C, 61.65; H, 8.90; O, 16.42; N, 5.75; Cl, 7.28%. Found: C, 61.40; H, 8.96; O, 16.21; N, 5.59; Cl, 7.27%.

3.5. Synthesis of **LH-DD-2Br**

To a suspension of **vin-DD** (2.0 g, 4.11 mmol) in ethanol (11 mL) was added 4-bromoaniline (2.12 g, 12.3 mmol) at room temperature under nitrogen. The suspension was refluxed for 20 h. The reaction mixture was cooled to 0 °C. The yellow precipitate was collected by filtration and dried in vacuum to afford the product as yellow powder without further purification (0.54 g, 20%). 1H NMR ($CDCl_3$): δ 12.63 (s, 1H), 7.92 (s, 2H), 7.46–7.43 (m, 4H), 7.27–7.25 (m, 2H), 7.02–7.00 (m, 4H), 6.92–6.90 (m, 2H), 3.99–3.95 (t, 2H, J = 6.4 Hz), 1.83–1.76 (quint. 2H), 1.46–1.27 (br, 18H), 0.90–0.87 (t, 3H, J = 7.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.8, 149.0, 145.4, 142.0, 132.4, 127.8, 127.5, 114.9, 110.1, 68.2, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 26.0, 22.7, 14.1. HRMS (ESI) $[M+H]^+$: Found, 637.1431; Calcd., 637.1435.

3.6. Synthesis of **LH-TEG-2Br**

To a solution of **vin-TEG** (5.50 g, 11.9 mmol) in ethanol (31 mL) was added 4-bromoaniline (8.21 g, 47.8 mmol) at room temperature under nitrogen. The suspension was refluxed for 20 h. The reaction mixture was cooled to room temperature, then extracted with CH_2Cl_2 three times. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with

hexane/ethyl acetate (2/1 to 1/1) as an eluent. The obtained oil was dried in vacuum. The brownish yellow oil was obtained as a mixture with unidentified impurities (crude yield: 2.0 g, 27%). ^1H NMR (CD_2Cl_2): δ 12.65 (s, 1H), 7.99 (s, 2H), 7.49–7.45 (m, 4H), 7.32–7.28 (m, 2H), 7.08–7.04 (m, 4H), 6.96–6.92 (m, 2H), 4.14–4.11 (m, 2H), 3.84–3.81 (2H, m), 3.70–3.67 (m, 2H), 3.64–3.59 (m, 4H), 3.52–3.50 (m, 2H), 3.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 159.3, 136.8, 132.3, 129.3, 121.8, 120.6, 114.6, 107.7, 72.3, 71.2, 70.9, 70.8, 69.8, 68.1, 59.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$: Found, 639.0461; Calcd., 639.0465.

3.7. Synthesis of **LH-2DTD-2Br**

To a suspension of **vin-2DTD** (1.10 g, 2.08 mmol) in ethanol (5.5 mL) was added 4-bromoaniline (1.43 g, 8.34 mmol) at room temperature under nitrogen. The suspension was refluxed for 21 h. The reaction mixture was cooled to room temperature, then extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with hexane/ethyl acetate (20/1) as an eluent. The obtained oil was dried in vacuum to afford the product as yellow oil (0.82 g, 49%). ^1H NMR (CD_2Cl_2): δ 12.68 (s, 1H), 7.98 (s, 2H), 7.49–7.45 (m, 4H), 7.39–7.27 (m, 2H), 7.07–7.05 (m, 4H), 6.92–6.90 (m, 2H), 3.86–3.84 (d, 2H, $J = 5.7$ Hz), 1.81–1.75 (m, 1H), 1.52–1.27 (br, 40H), 0.89–0.88 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.1, 149.0, 145.4, 132.4, 127.8, 127.5, 119.9, 116.6, 114.9, 110.2, 71.1, 38.0, 31.9, 31.4, 30.0, 29.7, 29.6, 29.3, 26.9, 22.7, 14.1. HRMS (ESI) $[\text{M}+\text{Na}]^+$: Found, 807.3468; Calcd., 807.3458.

3.8. Synthesis of **LB-DD-2Br**

To a solution of **LH-DD-2Br** (500 mg, 0.78 mmol) in toluene (11 mL) were added $\text{BF}_3 \cdot \text{OEt}_2$ (0.50 mL, 0.55 g, 3.9 mmol) and triethylamine (0.35 mL, 0.26 g, 2.6 mmol) at room temperature under nitrogen. The suspension was heated to 100 °C and stirred for 4 h. The reaction mixture was cooled to room temperature, then extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with toluene/hexane (1/1) as an eluent. The obtained oil was purified with HPLC, CHCl_3 as an eluent. The resulting oils were dissolved in small portion of CHCl_3 , and reprecipitated into hexane at -78 K. The precipitate was collected by suction filtration to get the product as yellow solid (0.32g, 59%). ^1H NMR (CD_2Cl_2): δ 7.93–7.88 (m, 2H), 7.59–7.55 (m, 4H), 7.39–7.36 (m, 4H), 7.28–7.25 (m, 2H), 6.95–6.91 (m, 2H), 3.98–3.94 (t, 2H, $J = 6.7$ Hz), 1.81–1.74 (quint., 2H, $J = 6.7$ Hz), 1.48–1.27 (br, 18H), 0.90–0.86 (t, 3H, $J = 7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.4, 153.7, 142.9, 132.4, 127.4, 127.8, 127.0, 125.6, 121.0, 115.2, 109.3, 68.2, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.78 (t, $J = 31.1$ Hz). HRMS (ESI) $[\text{M}+\text{Na}]^+$: Found, 711.1366; Calcd., 711.1362.

3.9. Synthesis of **LB-TEG-2Br**

To a solution of **LH-TEG-2Br** (2.00 g, 3.23 mmol) in toluene (43 mL) were added $\text{BF}_3 \cdot \text{OEt}_2$ (2.1 mL, 2.3 g, 16 mmol) and triethylamine (1.4 mL, 1.0 g, 10 mmol) at room temperature under nitrogen. The suspension was heated to 100 °C and stirred for 12 h. The reaction mixture was cooled to room temperature, then extracted with ethyl acetate

three times. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with hexane/ethyl acetate (1/1) as an eluent. The obtained oil was dried in vacuum to afford the product as orange oil (2.0 g, 93%). ¹H NMR (CD₂Cl₂): δ 7.92–7.90 (m, 2H), 7.59–7.55 (m, 4H), 7.40–7.37 (m, 4H), 7.30–7.26 (m, 2H), 6.98–6.94 (m, 2H), 4.14–4.11 (m, 2H), 3.83–3.81 (m, 2H), 3.69–3.66 (m, 2H), 3.63–3.58 (m, 4H), 3.51–3.49 (m, 2H), 3.33 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 158.4, 154.4, 143.4, 132.7, 128.7, 127.3, 126.1, 121.2, 115.6, 109.5, 72.3, 71.2, 70.9, 70.0, 68.1, 59.0. ¹¹B{¹H} NMR (CD₂Cl₂): δ 1.78 (t, *J* = 32.3 Hz). HRMS (ESI) [M+Na]⁺: Found, 687.0447; Calcd., 687.0447.

3.10. Synthesis of **LB-2DTD-2Br**

To a solution of **LH-2DTD-2Br** (0.80 g, 0.99 mmol) in toluene (13 mL) were added BF₃•OEt₂ (0.70 mL, 0.79 g, 5.6 mmol) and triethylamine (0.50 mL, 0.36 g, 3.6 mmol) at room temperature under nitrogen. The suspension was heated to 100 °C and stirred for 5 h. The reaction mixture was cooled to room temperature, then extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with hexane/ethyl acetate (20/1) as an eluent. The obtained oil was dried in vacuum to afford the product as orange oil (0.61 g, 72%). ¹H NMR (CD₂Cl₂): δ 7.98–7.88 (m, 2H), 7.59–7.55 (m, 4H), 7.39–7.36 (m, 4H), 7.27–7.25 (m, 2H), 6.95–6.92 (m, 2H), 3.85–3.84 (d, 2H, *J* = 5.7 Hz), 1.80–1.75 (m, 1H), 1.46–1.27 (br, 40H), 0.89–0.86 (m, 6H). ¹³C{¹H} NMR (CDCl₃): δ 158.7, 153.7, 142.9, 132.4, 127.8, 126.9, 125.6, 121.0, 115.3, 109.3, 71.2, 37.9, 31.9, 30.0, 29.7, 29.7,

29.6, 26.8, 22.7, 14.1. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.78 (t, $J = 31.5$ Hz). HRMS (ESI) $[\text{M}+\text{Na}]^+$: Found, 879.3242; Calcd., 879.3240.

*3.11. General procedure for the synthesis of conjugated polymer **PLB-R** ($R = \text{DD}$, TEG, and 2DTD)*

To a solution of $\text{Ni}(\text{cod})_2$ and 2,2'-bipyridyl in toluene/DMF was added 1,5-cyclooctadiene at room temperature in a glovebox under nitrogen. The suspension was heated to 60 °C and stirred for 30 minutes. To the mixture was added a solution of **LB-R-2Br**, then heated to 80 °C and stirred for 1 day. Purification methods were described in each section for the compounds.

*3.11a. Synthesis of **PLB-DD***

LB_DD_2Br (149 mg, 0.22 mmol), $\text{Ni}(\text{cod})_2$ (120 mg, 0.43 mmol), 2,2'-bipyridyl (67.9 mg, 0.43 mmol), and 1,5-cyclooctadiene (0.50 mL, 470 mg, 4.3 mmol), toluene (2 mL) and DMF (2 mL) were employed. After heating, the reaction mixture was dropped into MeOH (40 mL). The blackish green precipitate was collected by filtration, then the solid was added into 1M HCl aq. (15 mL). The orange solid was collected by filtration and dried in vacuum. The solid was purified with Soxhlet extractor using MeOH, EtOH, and chloroform as eluents. All volatiles of CHCl_3 fraction were removed with a rotary evaporator. The obtained solid was dissolved in a small amount of CHCl_3 , then poured into an excess amount of methanol. The precipitate was collected by filtration and dried in vacuum to afford the product as orange solid (88 mg, 77%). ^1H NMR (CD_2Cl_2): δ 8.03 (s, 2H), 7.73–7.71 (d, 4H, $J = 8.2$ Hz), 7.62–7.60 (d, 4H, $J = 7.9$ Hz), 7.33–7.31 (d, 2H, $J = 8.2$ Hz), 6.96–6.94 (d, 2H, $J = 7.9$ Hz), 3.99–3.95 (t, 3H, $J = 6.4$ Hz), 1.80–1.76 (m,

2H), 1.46–1.28 (br, 18H), 0.89–0.86 (t, 3H, $J = 6.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 158.7, 154.1, 144.0, 139.3, 128.7, 128.2, 127.2, 124.8, 115.5, 109.4, 68.6, 32.3, 30.1, 30.0, 30.0, 30.0, 29.8, 29.7, 29.7, 26.4, 23.1, 14.3. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.37 (t, $J = 32.5$ Hz).

3.11b. Synthesis of **PLB-TEG**

LB_TEG_2Br (130 mg, 0.20 mmol), $\text{Ni}(\text{cod})_2$ (107 mg, 0.39 mmol), 2,2'-bipyridyl (61.0 mg, 0.39 mmol), and 1,5-cyclooctadiene (0.05 mL, 44 mg, 0.41 mmol) in toluene (2 mL) and DMF (2 mL) were employed. After heating, the reaction mixture was dropped into MeOH (40 mL). The blackish green precipitate was collected by filtration, then the solid was added into 1M HCl aq. (15 mL). The orange solid was collected by filtration and dried in vacuum. The solid was purified with Soxhlet extractor using MeOH, EtOH, and chloroform as eluents. All volatiles of CHCl_3 fraction were removed with a rotary evaporator. The obtained solid was dissolved in a small amount of CHCl_3 , then poured into an excess amount of methanol. The precipitate was collected by filtration and dried in vacuum to afford the product as orange solid (77 mg, 78%). ^1H NMR (CD_2Cl_2): δ 8.03 (s, 2H), 7.74–7.72 (d, 4H, $J = 8.3$ Hz), 7.63–7.61 (d, 4H, $J = 8.0$ Hz), 7.35–7.33 (d, 2H, $J = 8.3$ Hz), 7.00–6.97 (d, 2H, $J = 9.0$ Hz), 4.16 (s, 2H), 3.80 (s, 2H), 3.64 (s, 2H), 3.60–3.57 (m, 4H), 3.49–3.47 (m, 2H), 3.29 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 158.4, 154.2, 144.0, 139.4, 129.2, 128.3, 127.3, 124.8, 115.6, 109.3, 72.3, 71.2, 70.9, 70.870.1, 68.1, 59.0. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.37 (t, $J = 31.9$ Hz).

3.11c. Synthesis of **PLB-2DTD**

LB_DD_2Br (170 mg, 0.20 mmol), $\text{Ni}(\text{cod})_2$ (109 mg, 0.40 mmol), 2,2'-bipyridyl

(62.0 mg, 0.40 mmol), and 1,5-cyclooctadiene (0.50 mL, 471 mg, 4.1 mmol) in toluene (1.5 mL) and DMF (1.5 mL) were employed. After heating, the reaction mixture was dropped into MeOH (40 mL). The blackish green precipitate was collected by filtration, then the solid was added into 1M HCl aq. (15 mL). The orange solid was collected by filtration and dried in vacuum. The solid was purified with Soxhlet extractor using MeOH, EtOH, and chloroform as eluents. All volatiles of CHCl₃ fraction were removed with a rotary evaporator. The obtained solid was dissolved in a small amount of CHCl₃, then poured into excess amount of methanol. The precipitate was collected by filtration and dried in vacuum to afford the product as orange solid (0.11 g, 83%). ¹H NMR (CD₂Cl₂): δ 8.03 (s, 2H), 7.75–7.72 (d, 4H, *J* = 8.8 Hz), 7.63–7.61 (d, 4H, *J* = 7.9 Hz), 7.34–7.32 (d, 2H, *J* = 8.2 Hz), 6.97–6.95 (d, 2H, *J* = 8.2 Hz), 3.87–3.86 (d, 2H, *J* = 5.5 Hz), 1.80–1.76 (m, 1H), 1.45–1.27 (br, 40H), 0.89–0.86 (t, 6H, *J* = 6.5 Hz). ¹³C{¹H} NMR (CD₂Cl₂): δ 159.0, 154.1, 144.0, 139.3, 128.6, 128.2, 127.2, 124.8, 115.5, 109.5, 71.6, 38.4, 32.3, 31.7, 30.4, 30.1, 30.1, 30.0, 29.7, 27.2, 23.1, 14.3. ¹¹B{¹H} NMR (CD₂Cl₂): δ 1.37 (t, *J* = 32.5 Hz).

3.12. Synthesis of **LH-DD**

To a suspension of **vin-DD** (2.0 g, 4.11 mmol) in ethanol (11 mL) was added aniline (1.2 mL, 1.2 g, 13 mmol) at room temperature under nitrogen. After adding ten drops of acetic acid, the suspension was refluxed for 15 h. The reaction mixture was extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The mixture was filtered, and all volatiles were removed with a rotary evaporator. The resulting mixture was purified by silica gel chromatography with hexane/ethyl acetate (15/1) as an eluent. The obtained solid was dissolved in a small

amount of CHCl_3 , then poured into an excess amount of methanol. The precipitate was collected by filtration and dried in vacuum to afford the product as yellow powder (0.61 g, 31%). ^1H NMR (CDCl_3): δ = 12.74 (s, 2H), 8.00 (s, 2H), 7.37–7.33 (m, 4H), 7.30–7.28 (m, 2H), 7.16–7.13 (m, 4H), 6.93–6.90 (m, 2H), 3.99–3.96 (t, 2H, J = 6.6 Hz), 1.83–1.76 (quint., 2H, J = 7.2 Hz), 1.47–1.27 (m, 16H), 0.90–0.87 (t, 3H, J = 6.3 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.9, 148.9, 146.6, 132.6, 129.4, 127.4, 123.6, 118.3, 114.8, 109.4, 68.2, 31.9, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 26.0, 22.7, 14.1.

3.13. Synthesis of **LH-TEG**

To a suspension or a solution of **vin-TEG** (1.81 g, 3.89 mmol) in ethanol (10 mL) was added aniline (1.1 mL, 1.10 g, 11.7 mmol) at room temperature under nitrogen. After adding five drops of acetic acid, the suspension was refluxed for 14.5 h. The reaction mixture was added aniline (0.35 mL), then continued to reflux for 6.5 h. The mixture was cooled to room temperature, then extracted with ethyl acetate three times. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The mixture was filtered, and all volatiles were removed with a rotary evaporator. The resulting mixture was purified by silica gel chromatography with $\text{CHCl}_3/\text{MeOH}$ (80/1) and hexane/ethyl acetate (1/1) as an eluent. The obtained oil was dried in vacuum. The yellow oil was obtained as a mixture with unidentified impurities (crude yield: 0.13 g, 7%). ^1H NMR (CDCl_3): δ 12.73 (s, 1H), 8.00 (s, 2H), 7.37–7.33 (m, 4H), 7.30–7.28 (m, 2H), 7.16–7.14 (m, 4H), 7.11–7.07 (m, 2H), 6.96–6.93 (m, 2H), 4.17 (m, 2H), 3.89–3.86 (m, 2H), 3.77–3.75 (m, 2H), 3.71–3.66 (m, 6H), 3.57–3.55 (m, 2H), 3.39 (s, 3H). HRMS (ESI) $[\text{M}+\text{H}]^+$: Found, 461.2431; Calcd., 461.2435.

3.14. Synthesis of **LB-DD**

To a solution of **LH-DD** (838 mg, 1.74 mmol) in toluene (23 mL) were added $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 mL, 1.2 g, 8.7 mmol) and triethylamine (0.73 mL, 0.53 g, 5.2 mmol) at room temperature under nitrogen. The suspension was heated to 100 °C and stirred. The reaction mixture was cooled to room temperature, then extracted with CH_2Cl_2 three times. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with hexane/ethyl acetate (10/1) and toluene/hexane (3/1) as eluents. The obtained solid was dissolved in a small amount of toluene, then poured into an excess amount of methanol at -78 °C. The precipitate was collected by filtration and dried in vacuum to afford the product as yellow powder (267 mg, 29%). ^1H NMR (CD_2Cl_2): δ 12.74 (s, 1H), 8.00 (s, 2H), 7.37–7.33 (m, 4H), 7.30–7.28 (m, 2H), 7.16–7.13 (m, 4H), 7.11–7.07 (m, 2H), 6.93–6.90 (m, 2H), 3.99–3.96 (t, 2H, $J = 6.5$ Hz), 1.83–7.76 (quint. 2H, $J = 6.7$ Hz), 1.47–1.27 (br, 18H), 0.90–0.87 (t, 3H, $J = 6.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 158.6, 154.5, 144.6, 129.6, 128.8, 127.5, 127.1, 124.5, 115.4, 109.3, 68.6, 32.3, 30.0, 30.0, 30.0, 30.0, 29.8, 29.7, 29.7, 26.4, 23.1, 14.3. $^{11}\text{B}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.30 (t, $J = 31.5$ Hz). HRMS (ESI) $[\text{M}+\text{Na}]^+$: Found, 553.3177; Calcd., 553.3172.

3.15. Synthesis of **LB-TEG**

To a solution of **LH-TEG** (122 mg, 0.27 mmol) in toluene (3.5 mL) were added $\text{BF}_3 \cdot \text{OEt}_2$ (0.18 mL, 200 mg, 1.4 mmol) and triethylamine (0.15 mL, 110 mg, 1.1 mmol) at room temperature under nitrogen. The suspension was heated to 100 °C and stirred. The reaction mixture was cooled to room temperature, then extracted with CH_2Cl_2 three times.

The organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solution was filtered, and all volatiles were removed with a rotary evaporator. The mixture was purified by silica gel column chromatography with hexane/ethyl acetate (1/1) as an eluent. The obtained oil was dried in vacuum to afford the product as greenish yellow oil (7.2 mg, 5%). ¹H NMR (CD₂Cl₂): δ 7.96–7.94 (m, 2H), 7.51–7.43 (m, 8H), 7.38–7.29 (m, 4H), 6.98–6.95 (m, 2H), 4.14–4.12 (m, 2H), 3.84–3.81 (m, 2H), 3.69–3.66 (m, 2H), 3.63–3.58 (m, 4H), 3.52–3.49 (m, 2H), 3.33 (s, 3H). ¹³C {¹H} NMR (CD₂Cl₂): δ 158.2, 154.4, 144.6, 129.6, 129.2, 127.5, 127.1, 124.4, 115.5, 108.8, 72.3, 71.2, 70.9, 70.8, 70.0, 68.0, 59.0. ¹¹B {¹H} NMR (CD₂Cl₂): δ 1.37 (t, *J* = 31.3 Hz). HRMS (ESI) [M+H]⁺: Found, 531.2243; Calcd., 531.2237.

4. NMR Spectra

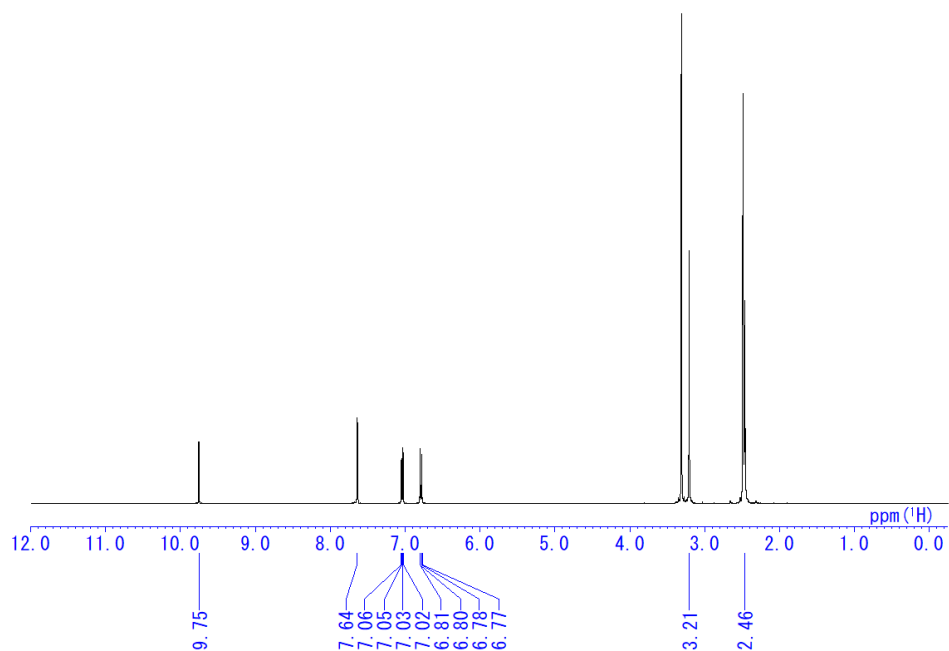


Chart S1. ¹H NMR spectrum of **vin-OH** in DMSO-d₆.

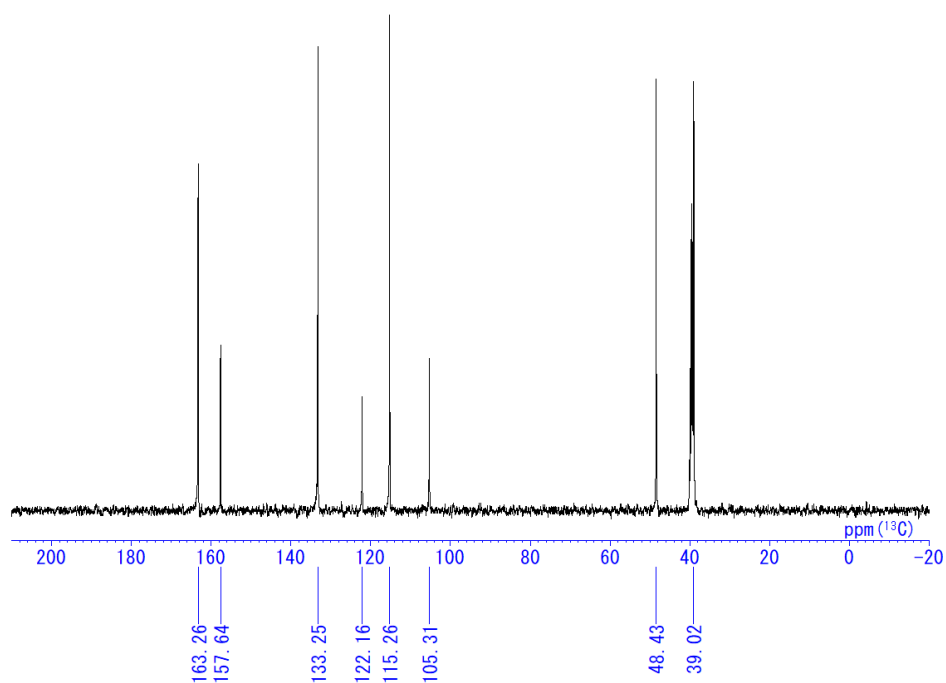


Chart S2. ¹³C{¹H} NMR spectrum of **vin-OH** in DMSO-d₆.

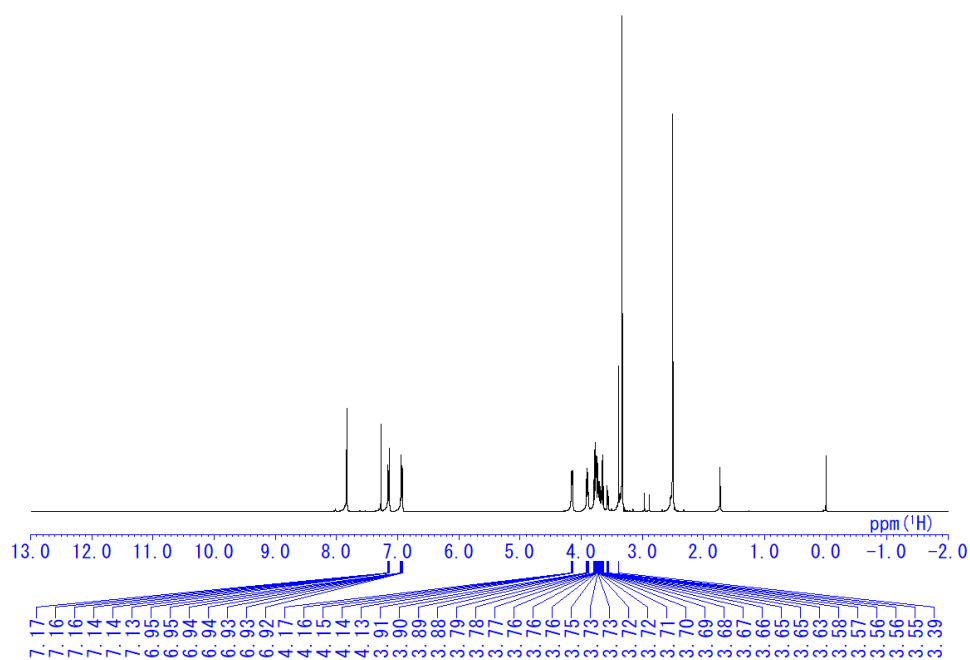


Chart S3. ^1H NMR spectrum of **vin-TEG** in CDCl_3 .

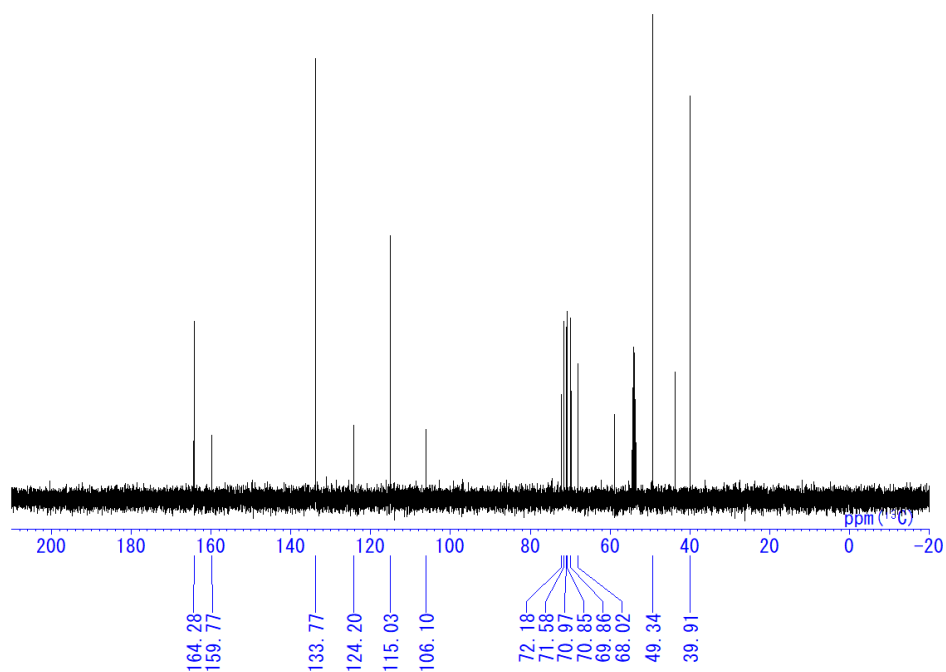


Chart S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **vin-TEG** in CDCl_3 .

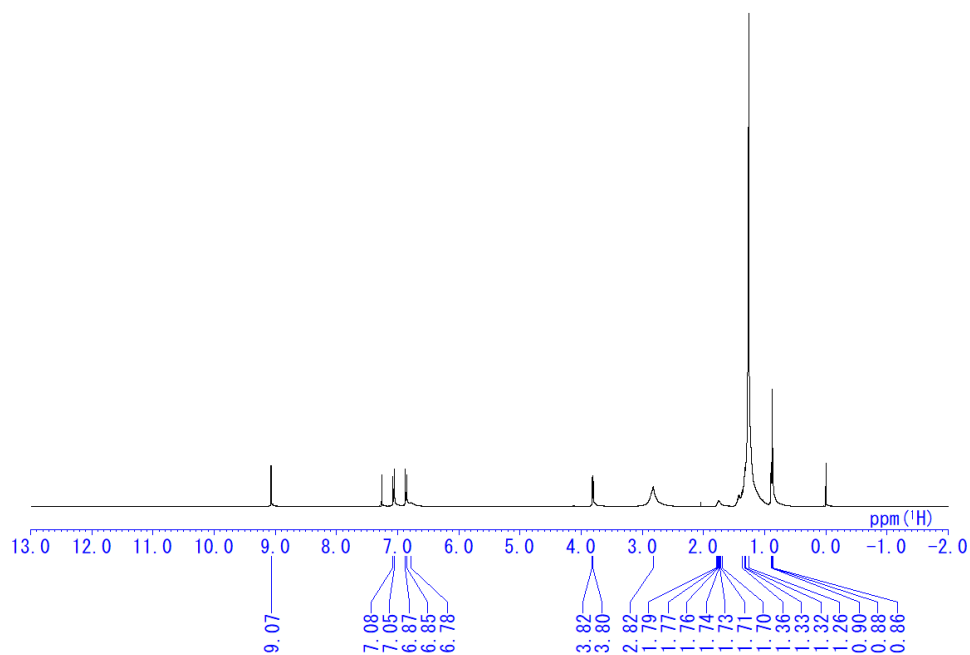


Chart S5. ^1H NMR spectrum of **vin-2DTD** in CDCl_3 .

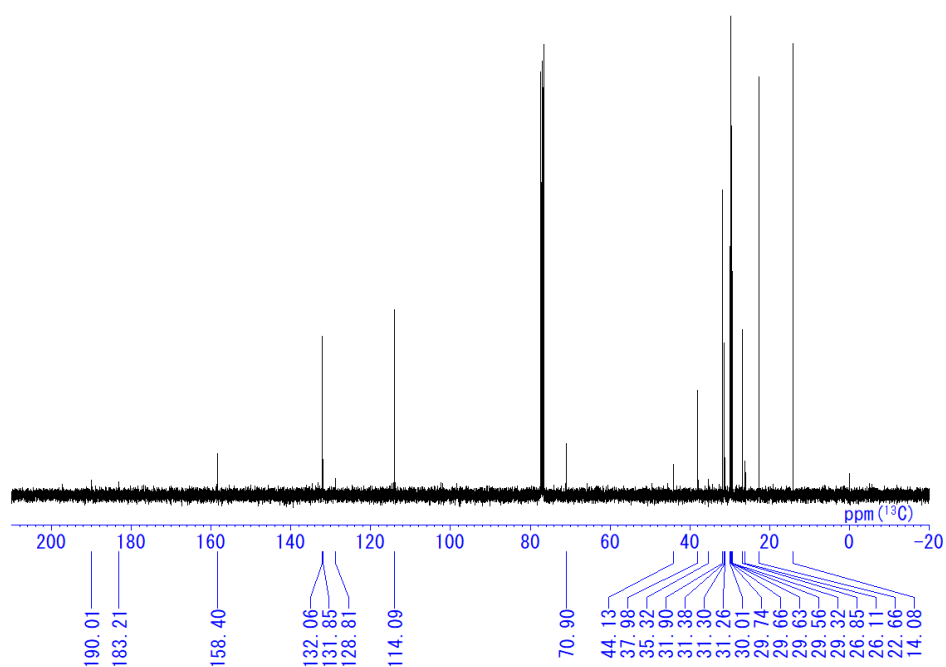


Chart S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **vin-2DTD** in CDCl_3 .

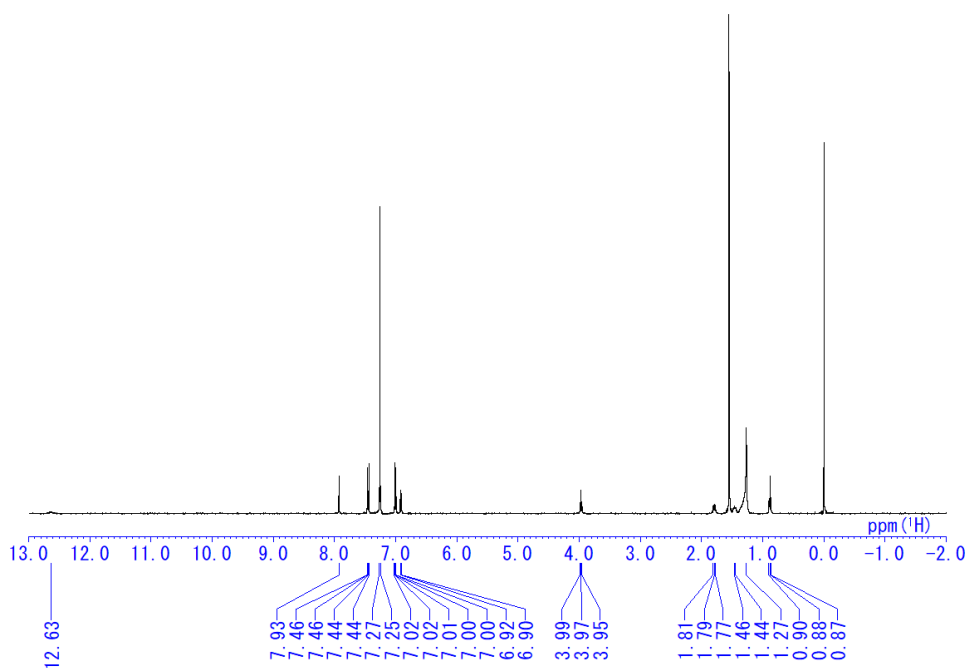


Chart S7. ¹H NMR spectrum of **LH-DD-2Br** in CDCl₃.

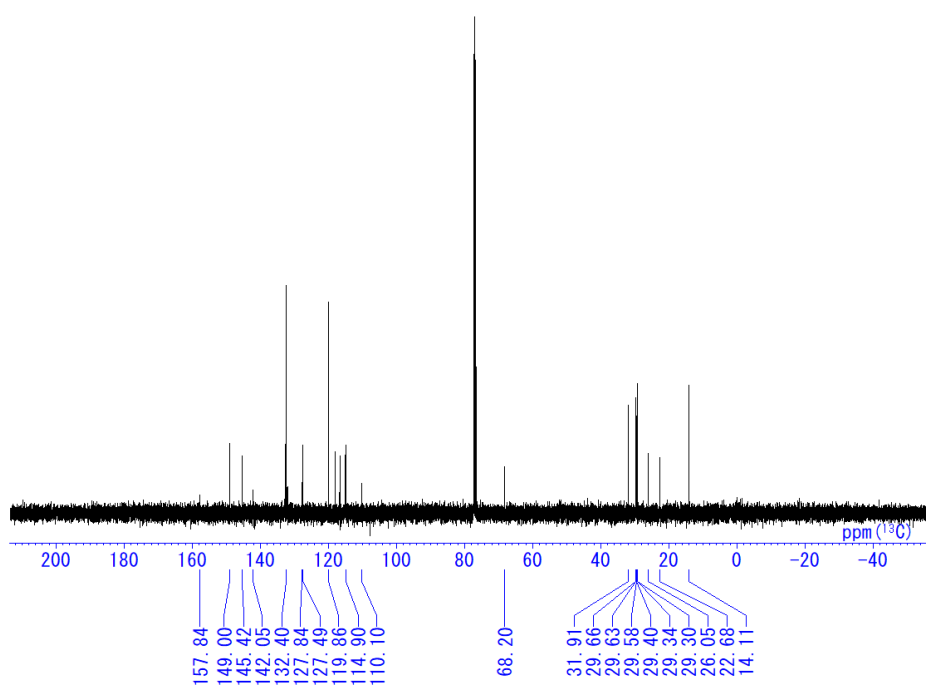


Chart S8. ¹³C{¹H} NMR spectrum of **LH-DD-2Br** in CDCl₃.

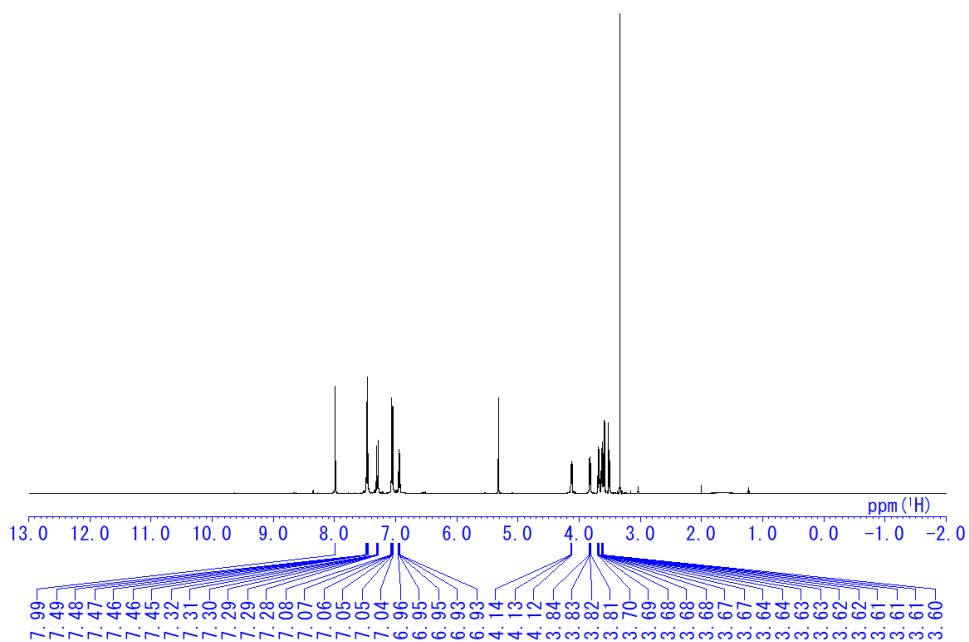


Chart S9. ^1H NMR spectrum of LH-TEG-2Br in CD_2Cl_2 .

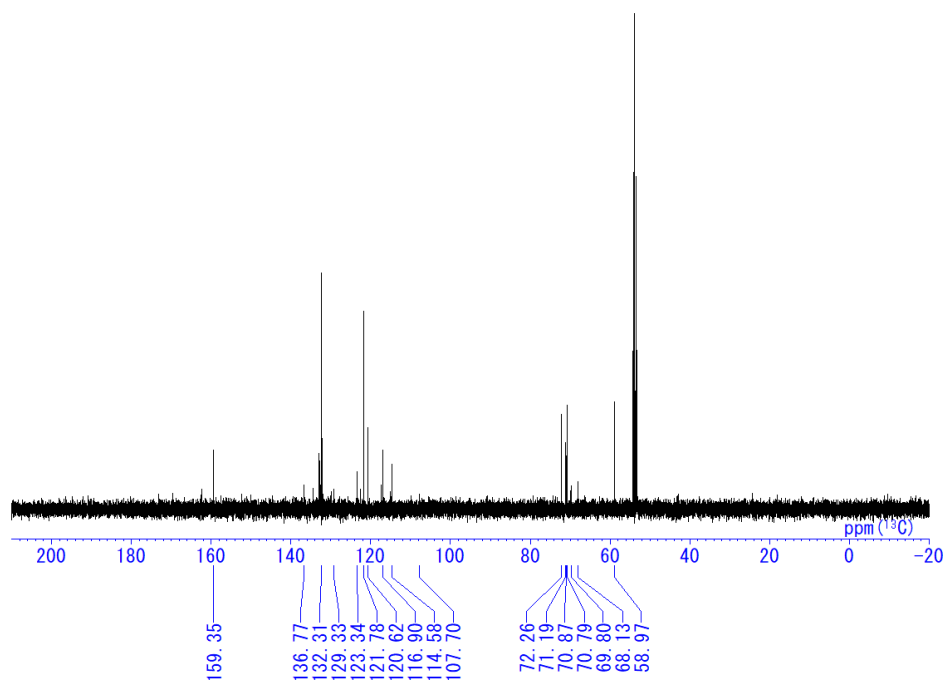


Chart S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of LH-TEG-2Br in CDCl_3 .

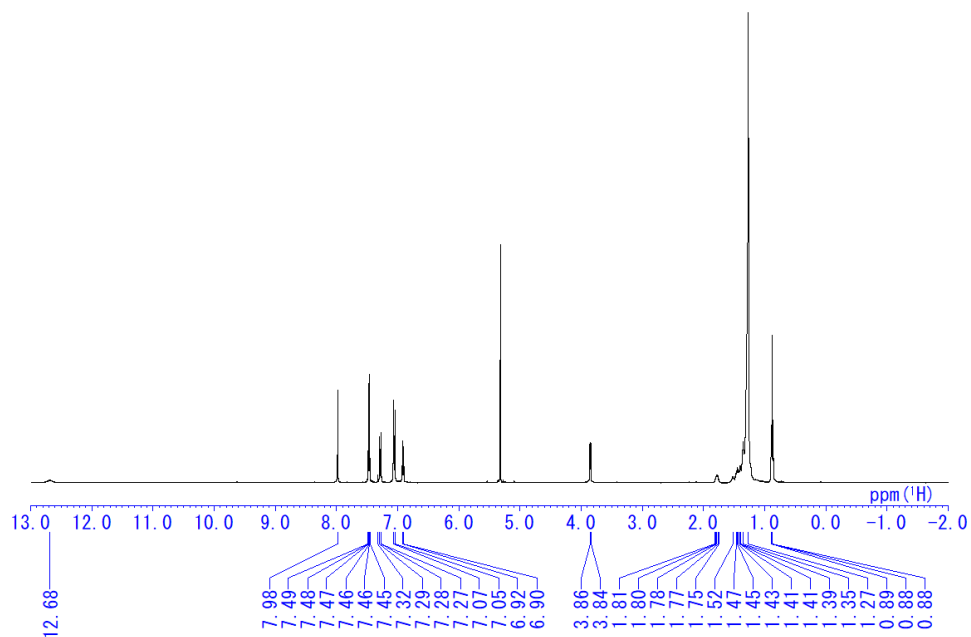


Chart S11. ^1H NMR spectrum of **LH-2DTD-2Br** in CD_2Cl_2 .

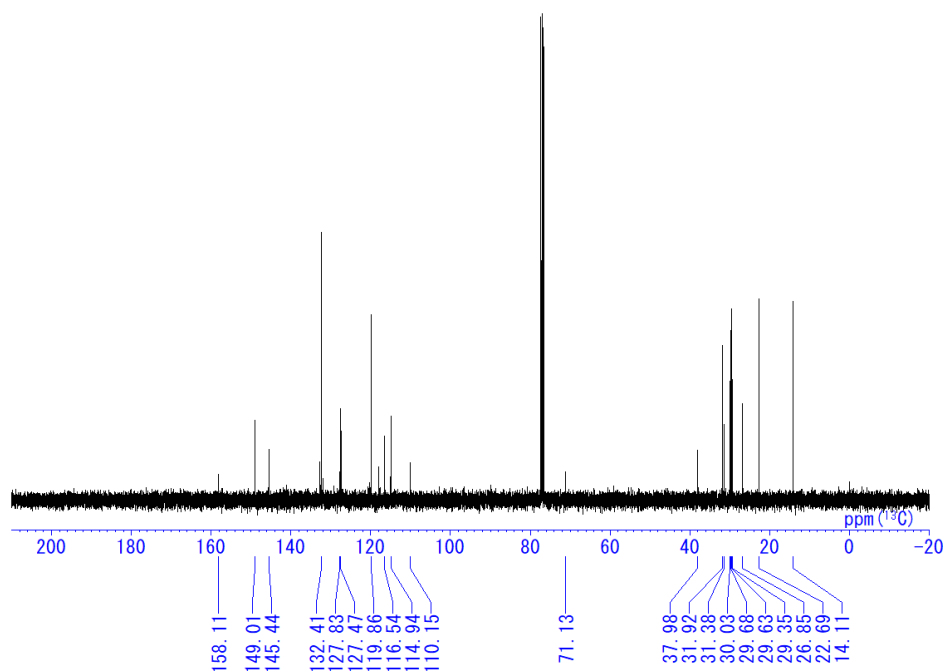


Chart S12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LH-2DTD-2Br** in CDCl_3 .

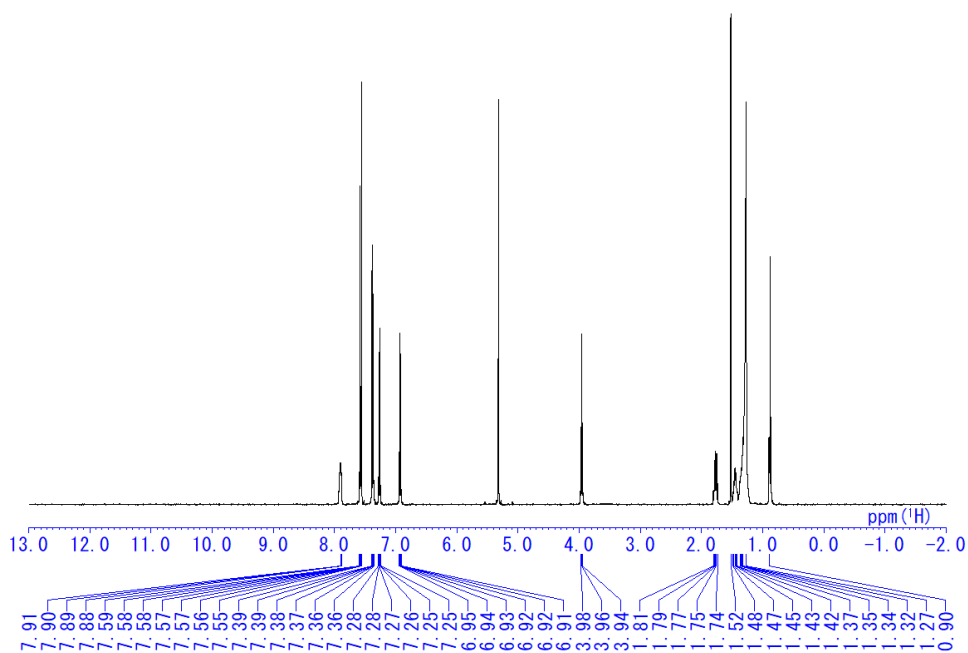


Chart S13. ^1H NMR spectrum of **LB-DD-2Br** in CD_2Cl_2 .

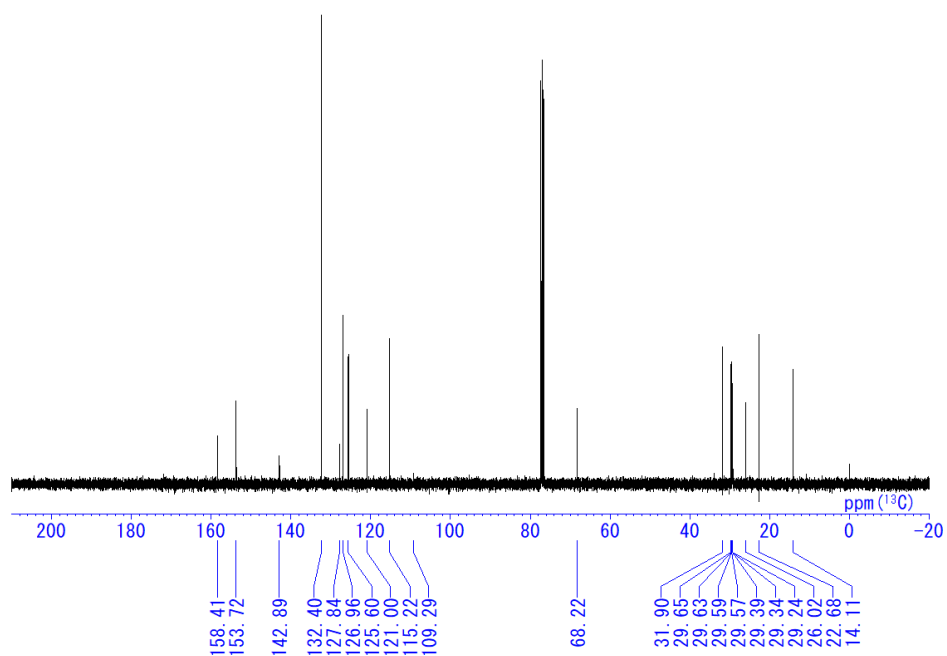


Chart S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LB-DD-2Br** in CDCl_3 .

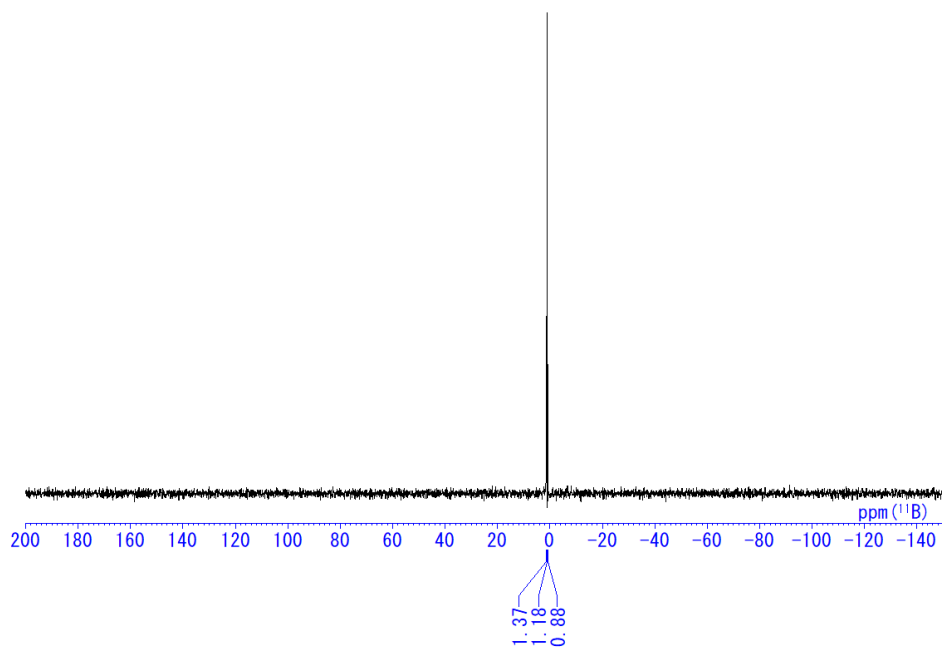


Chart S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **LB-DD-2Br** in CD_2Cl_2 .

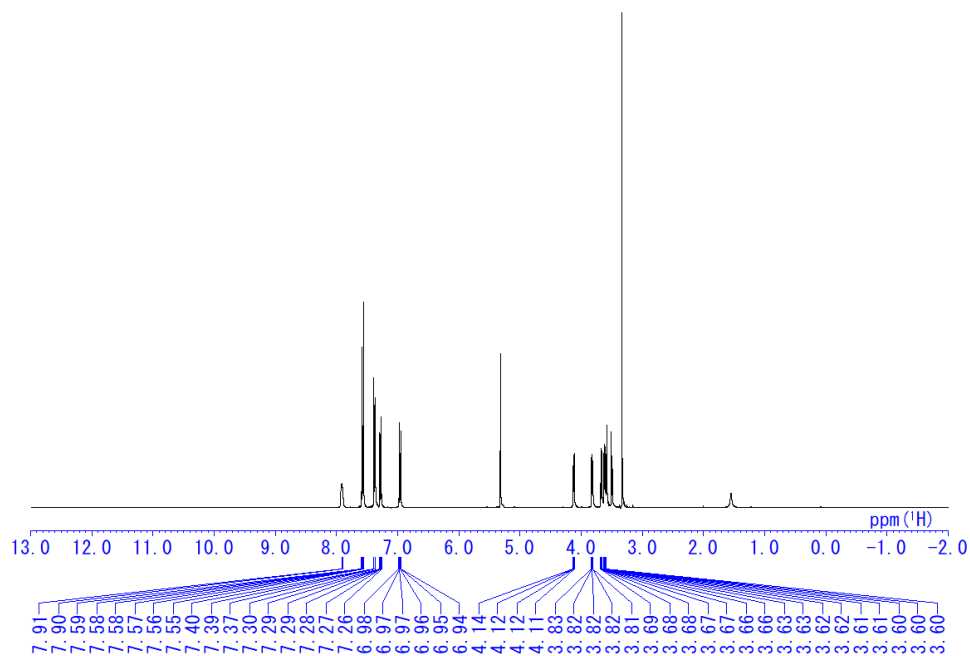


Chart S16. ^1H NMR spectrum of **LB-TEG-2Br** in CD_2Cl_2 .

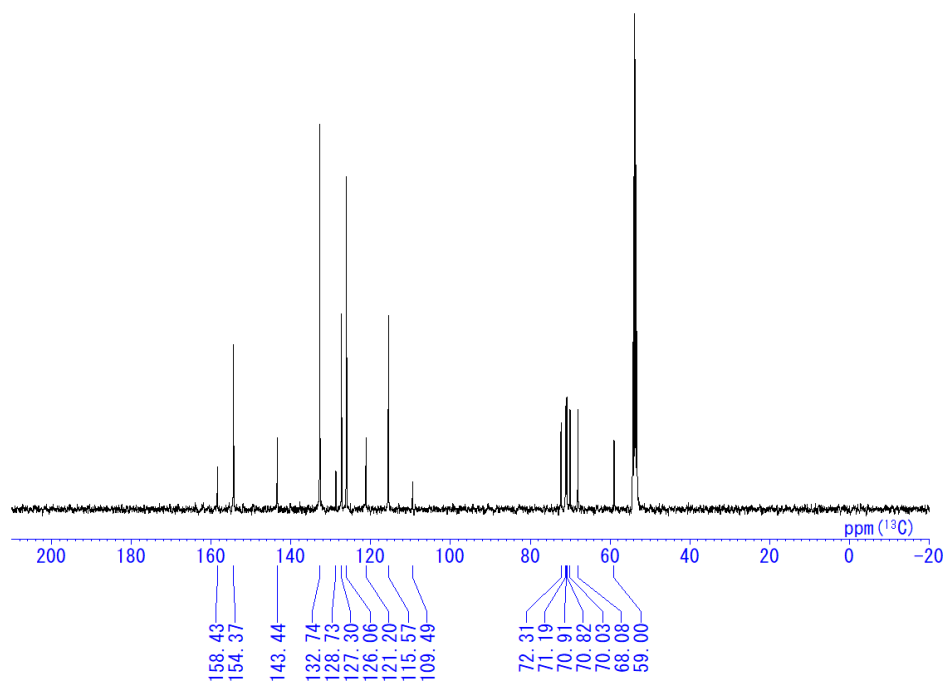


Chart S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LB-TEG-2Br** in CD_2Cl_2 .

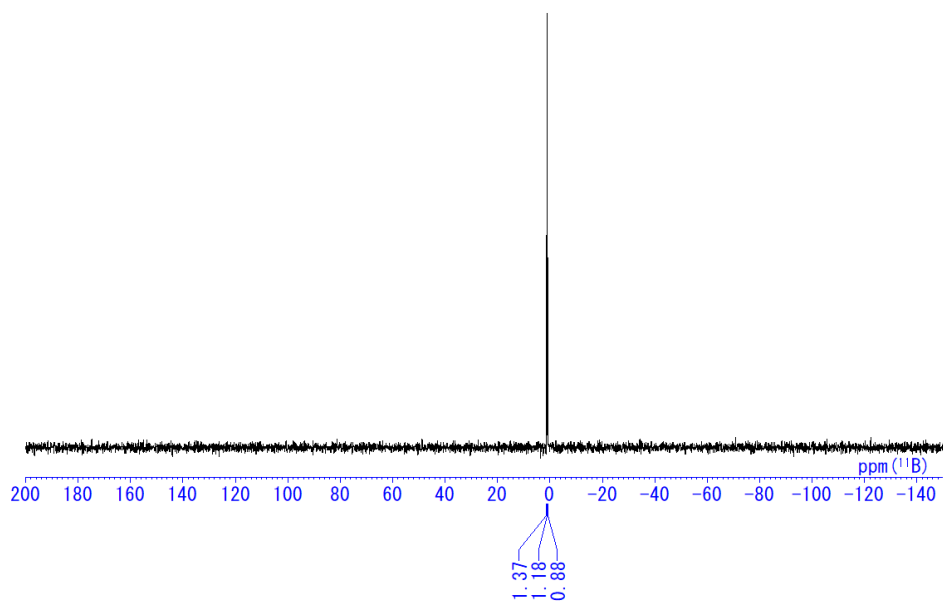


Chart S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **LB-TEG-2Br** in CD_2Cl_2 .

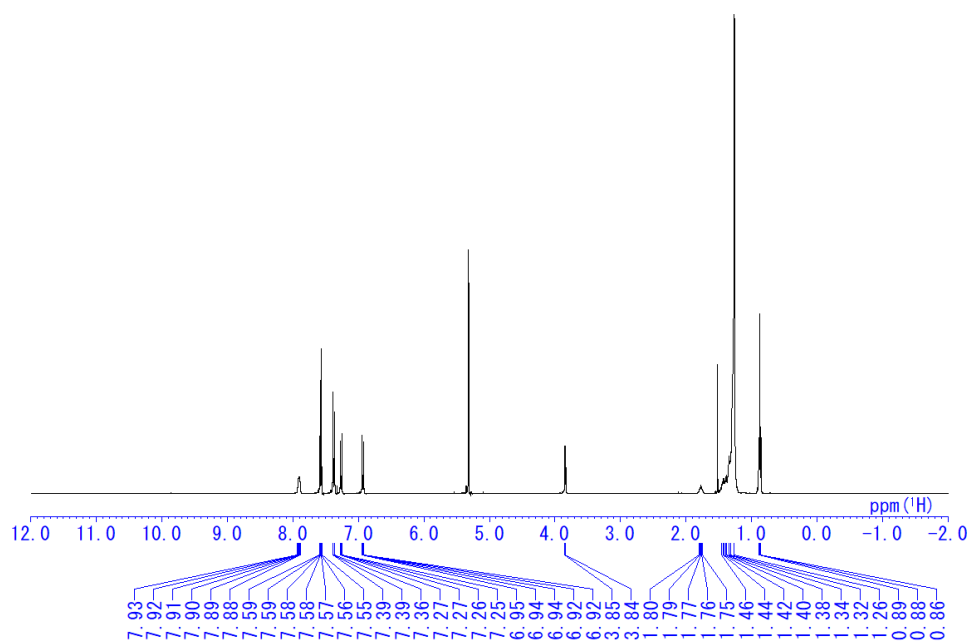


Chart S19. ^1H NMR spectrum of **LB-2DTD-2Br** in CD_2Cl_2 .

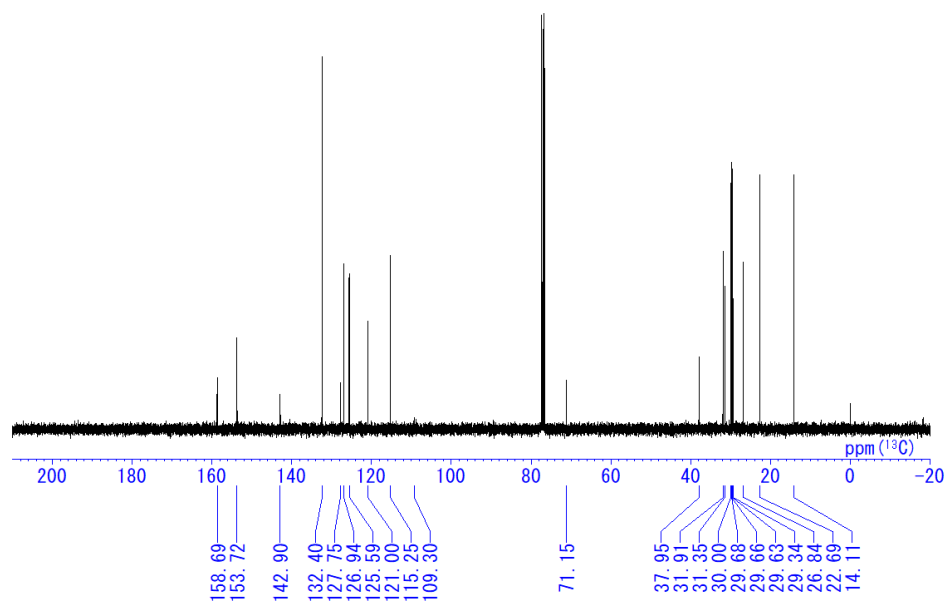


Chart S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LB-2DTD-2Br** in CDCl_3 .

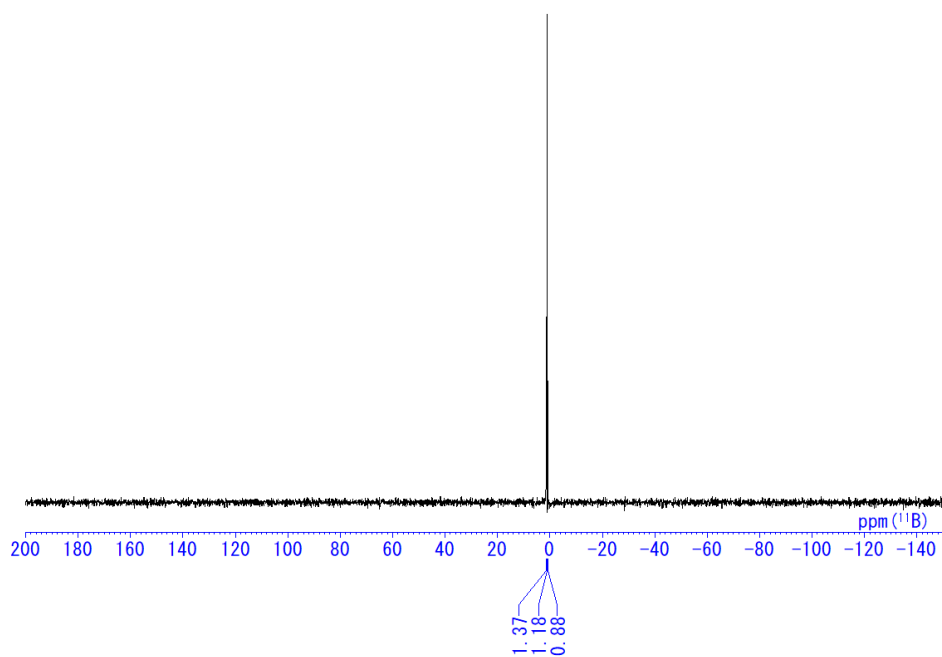


Chart S21. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **LB-2DTD-2Br** in CD_2Cl_2 .

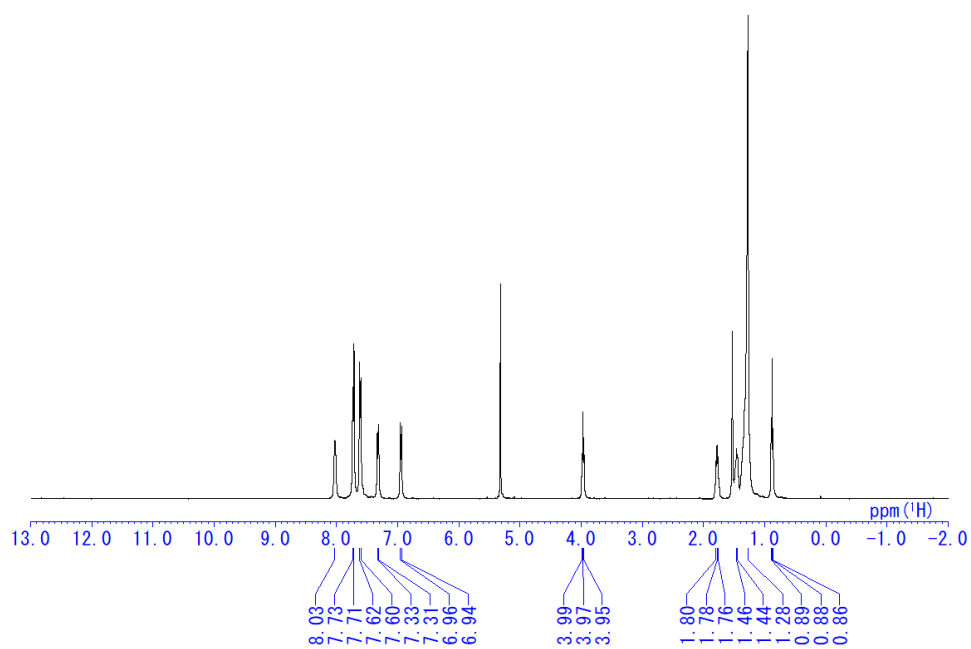


Chart S22. ^1H NMR spectrum of **PLB-DD** in CD_2Cl_2 .

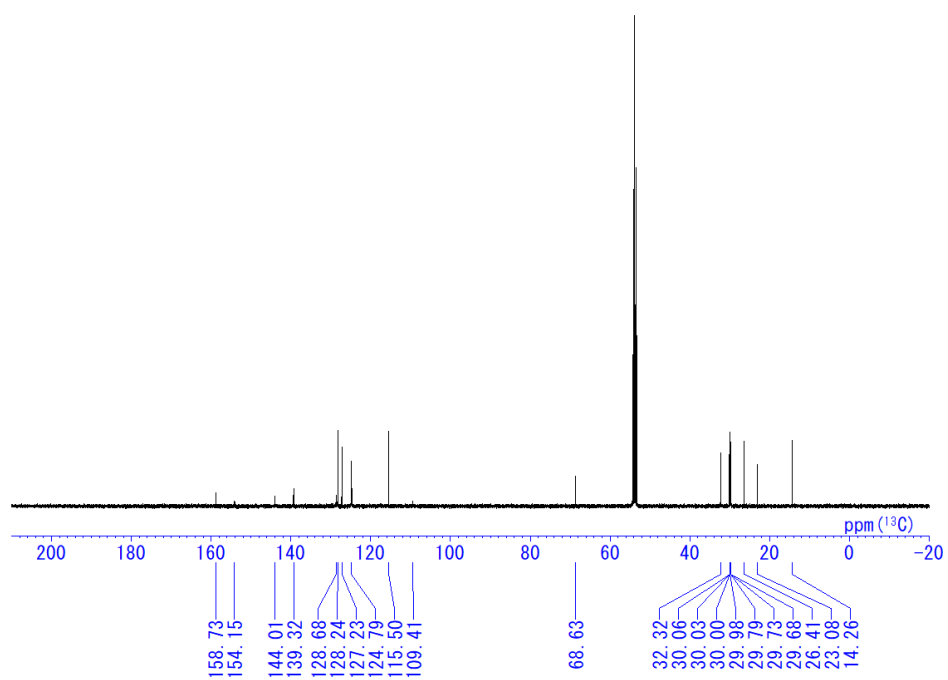


Chart S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **PLB-DD** in CD_2Cl_2 .

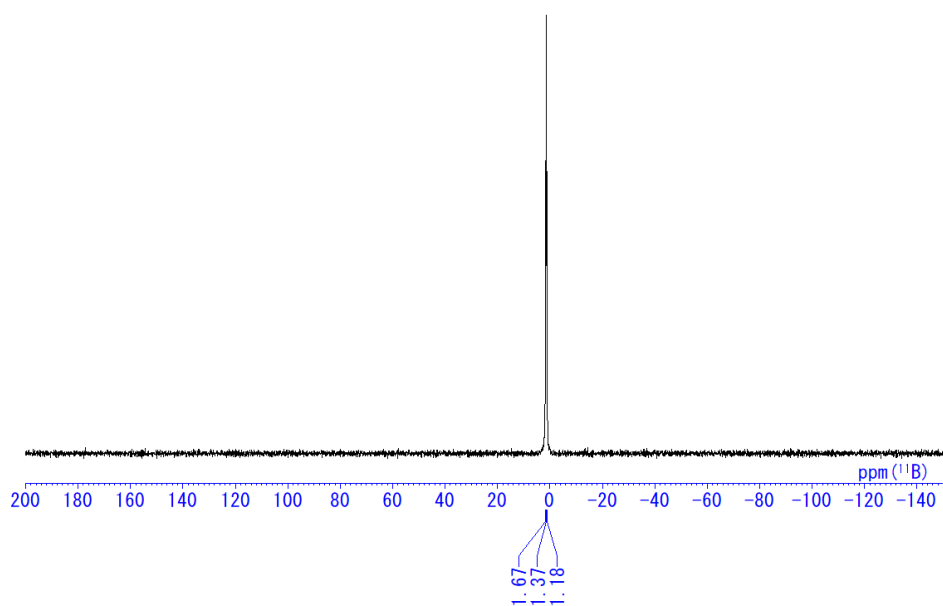


Chart S24. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **PLB-DD** in CD_2Cl_2 .

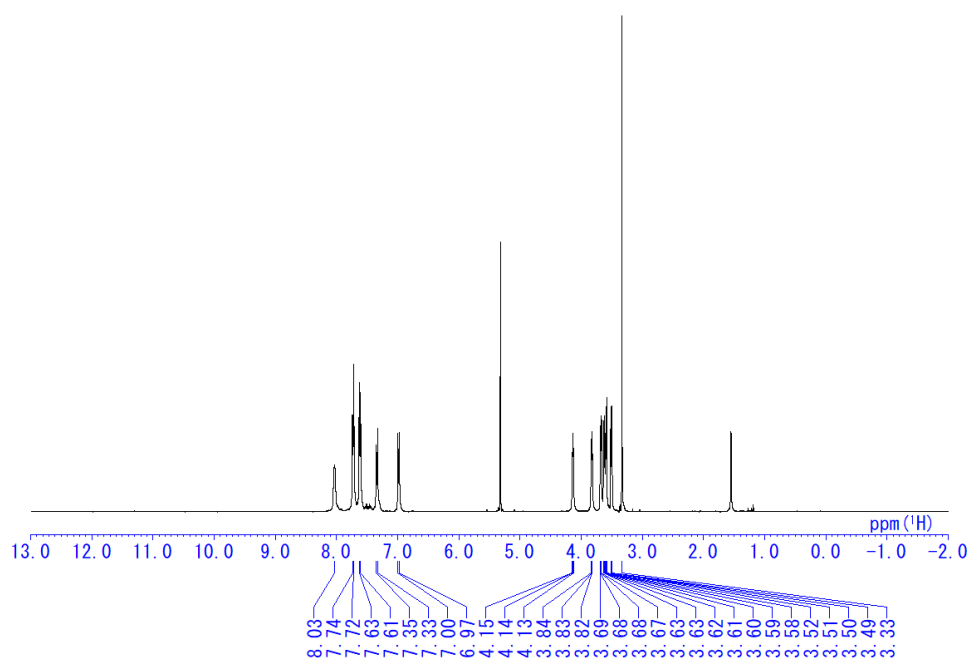


Chart S25. ^1H NMR spectrum of **PLB-TEG** in CD_2Cl_2 .

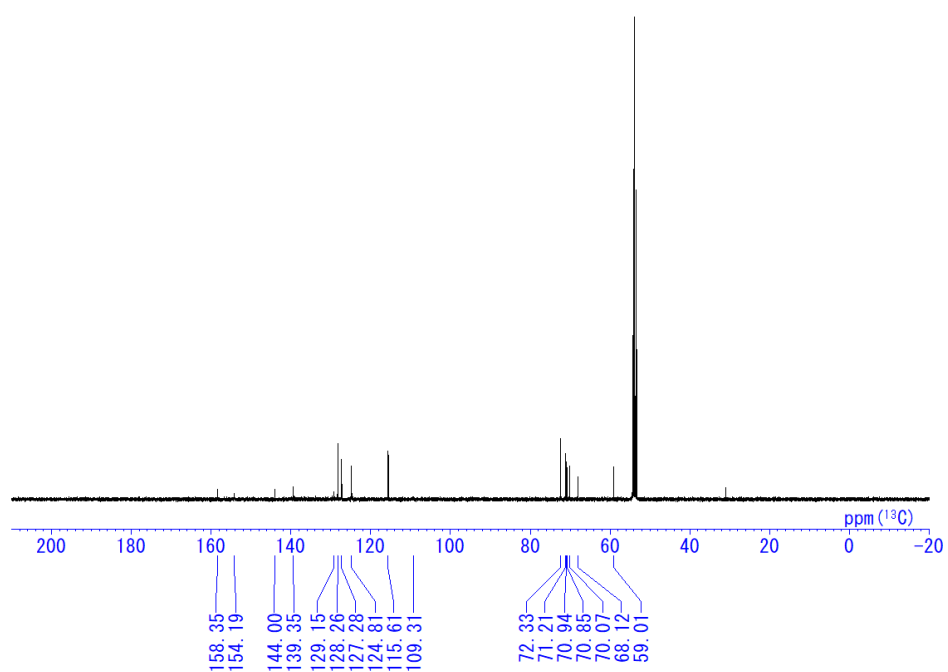


Chart S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **PLB-TEG** in CD_2Cl_2 .

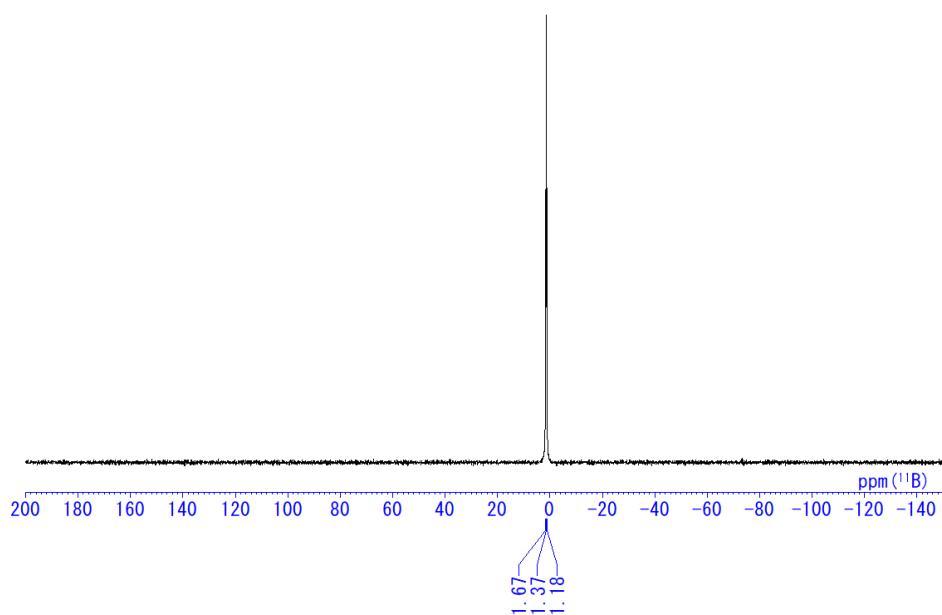


Chart S27. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **PLB-TEG** in CD_2Cl_2 .

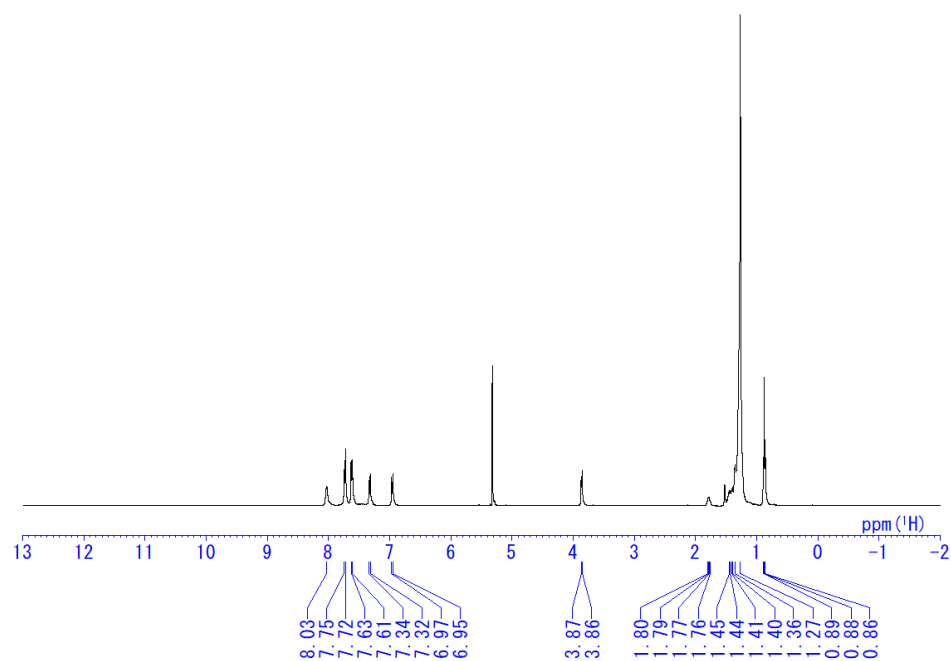


Chart S28. ^1H NMR spectrum of **PLB-2DTD** in CD_2Cl_2 .

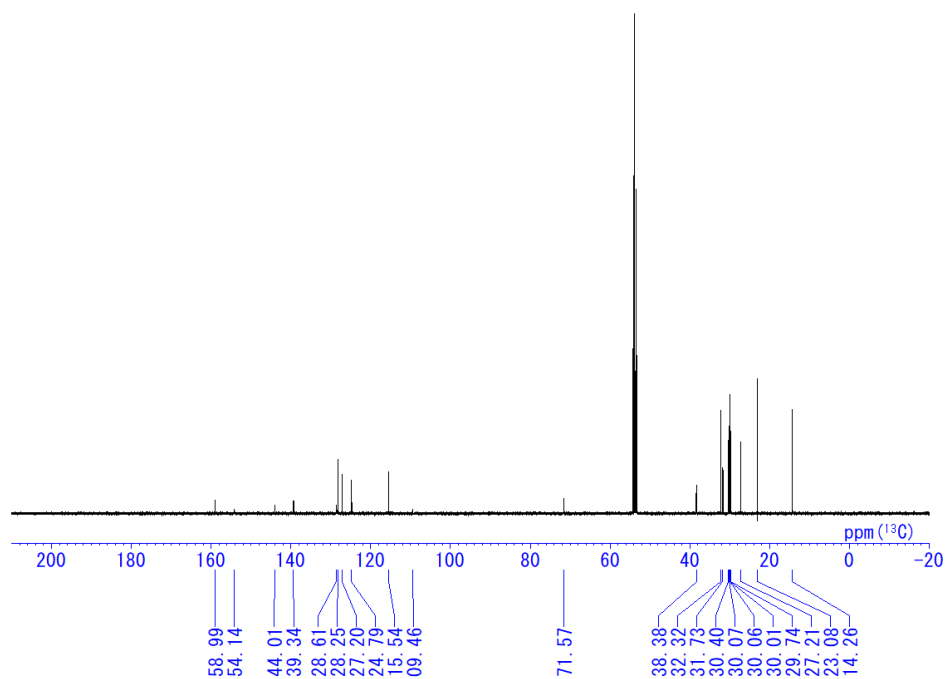


Chart S29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **PLB-2DTD** in CD_2Cl_2 .

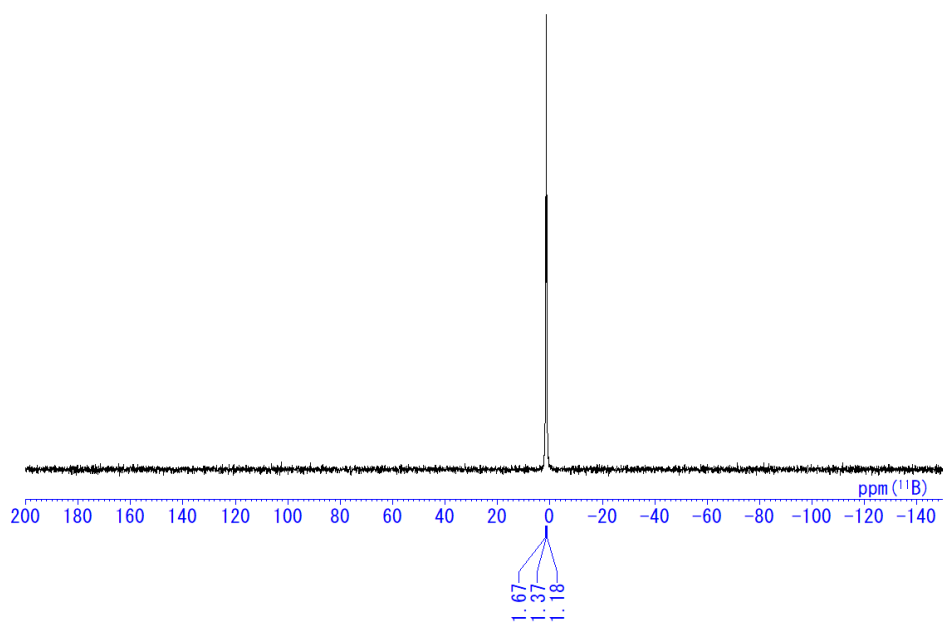


Chart S30. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **PLB-2DTD** in CD_2Cl_2 .

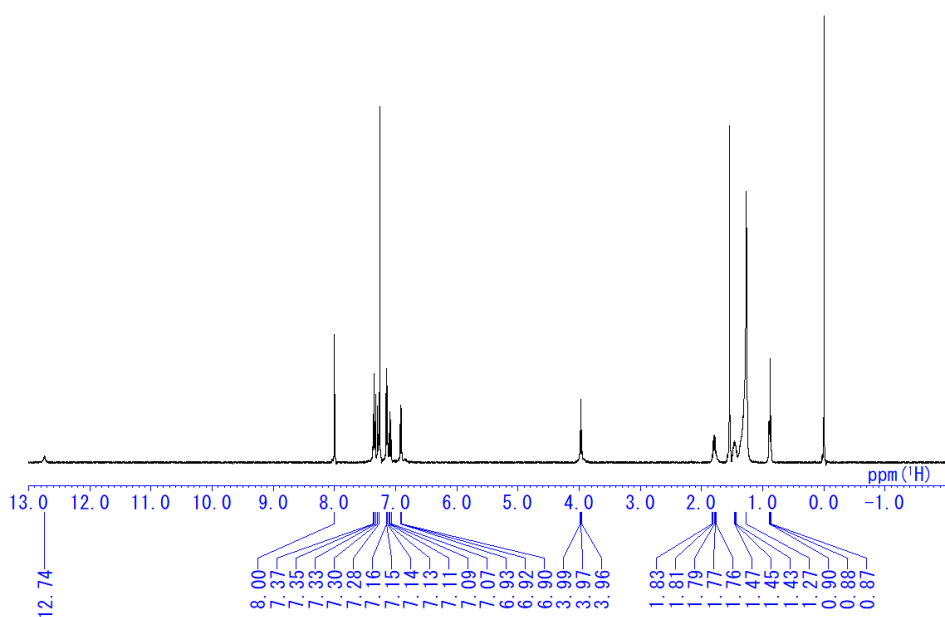


Chart S31. ^1H NMR spectrum of **LH-DD** in CDCl_3 .

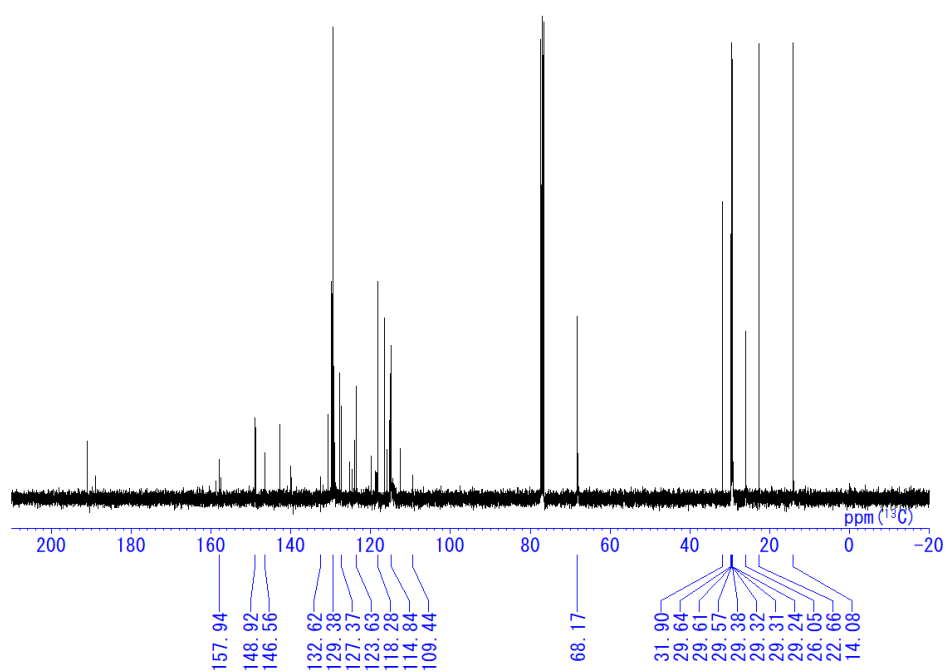
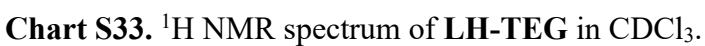


Chart S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LH-DD** in CDCl_3 .



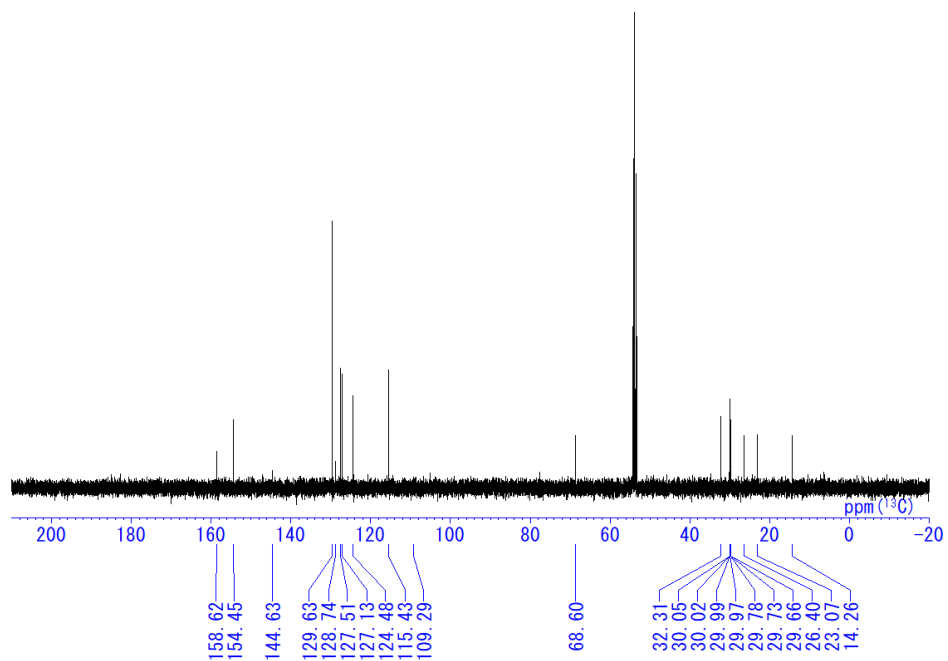


Chart S35. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LB-DD** in CD_2Cl_2 .

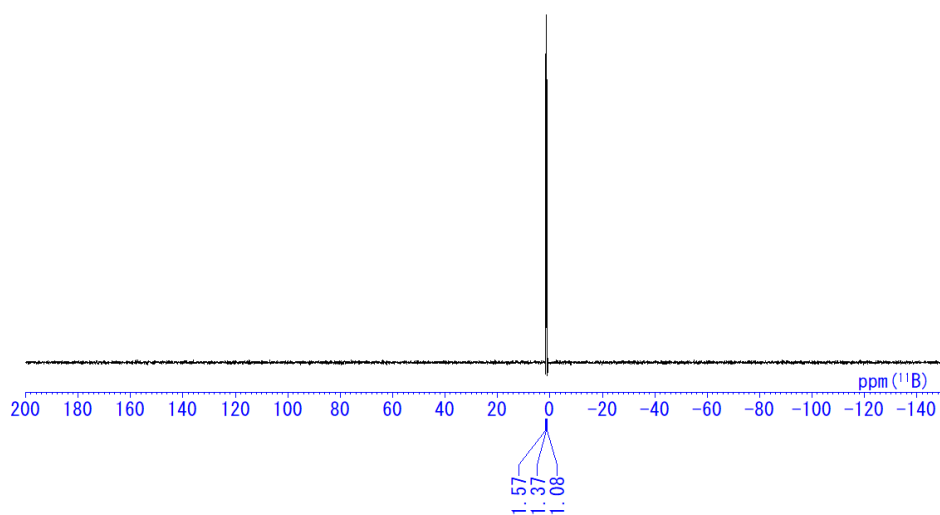


Chart S36. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **LB-DD** in CD_2Cl_2 .

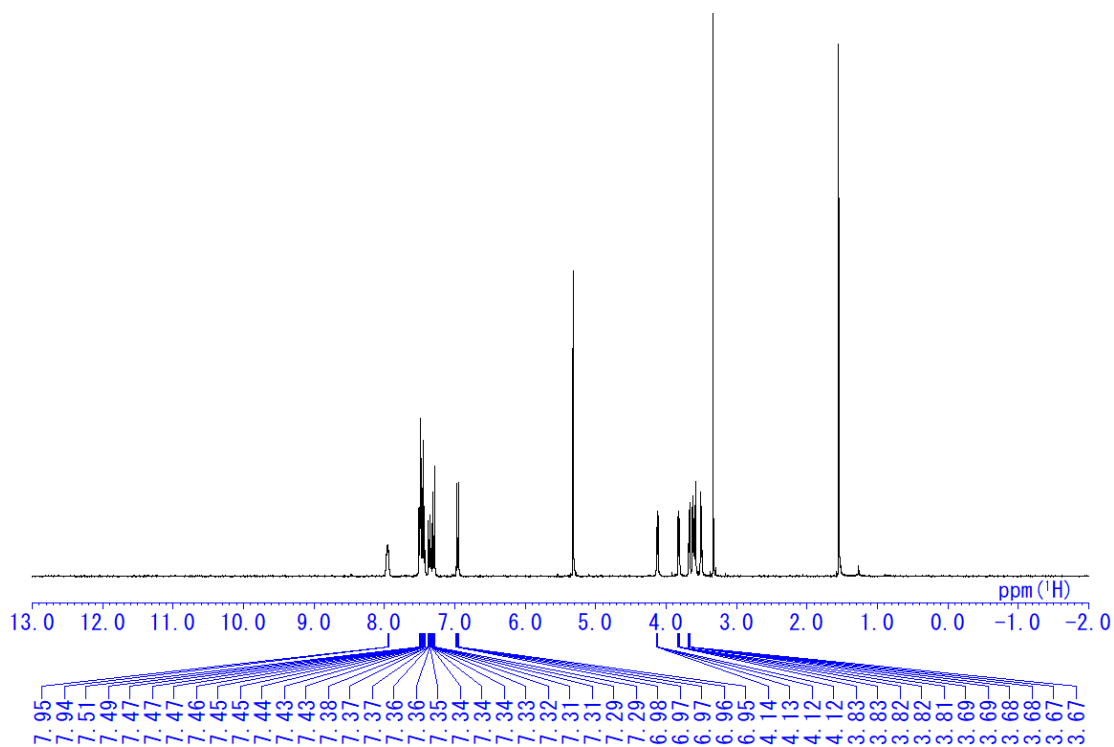


Chart S37. ^1H NMR spectrum of **LB-TEG** in CD_2Cl_2 .

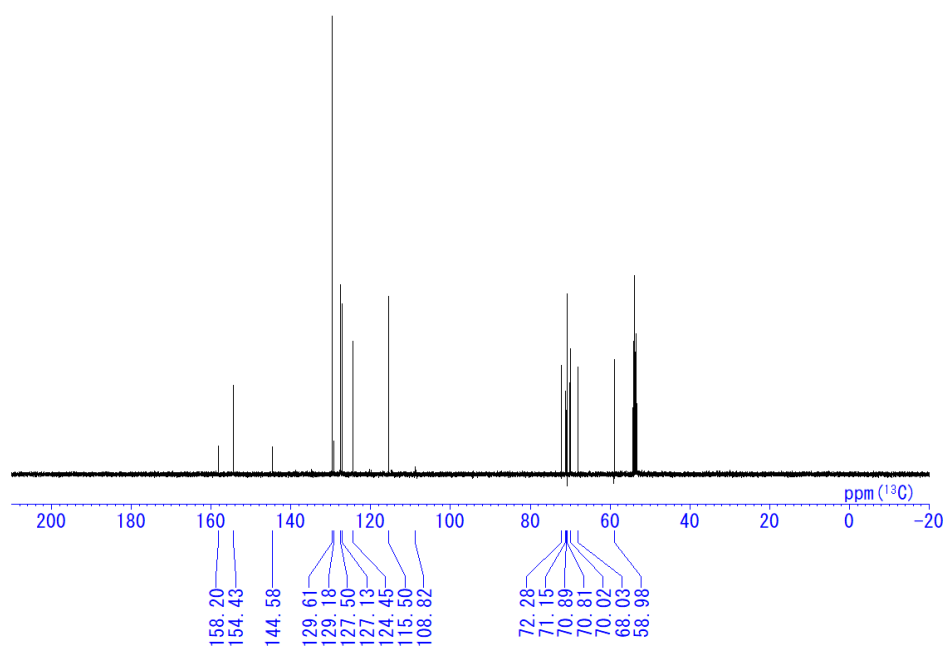


Chart S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **LB-TEG** in CD_2Cl_2 .

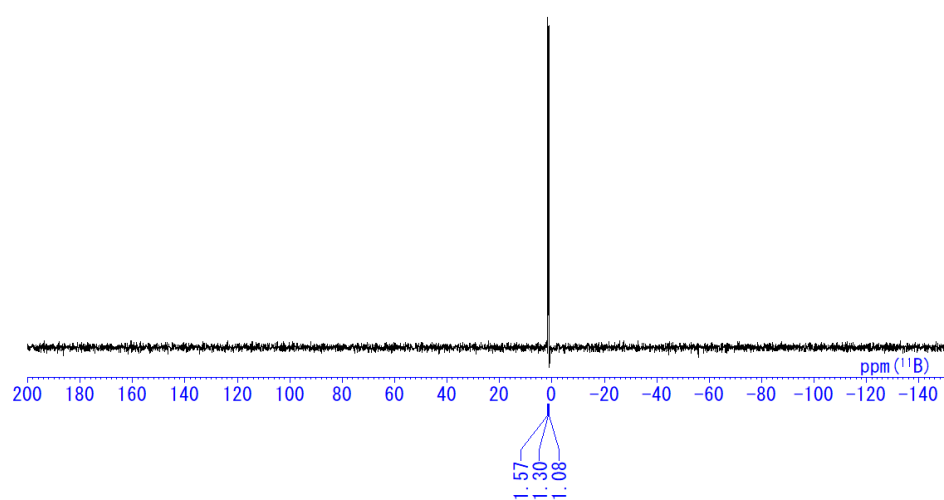


Chart S39. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **LB-TEG** in CD_2Cl_2 .

5. Photophysical Properties in Solid States

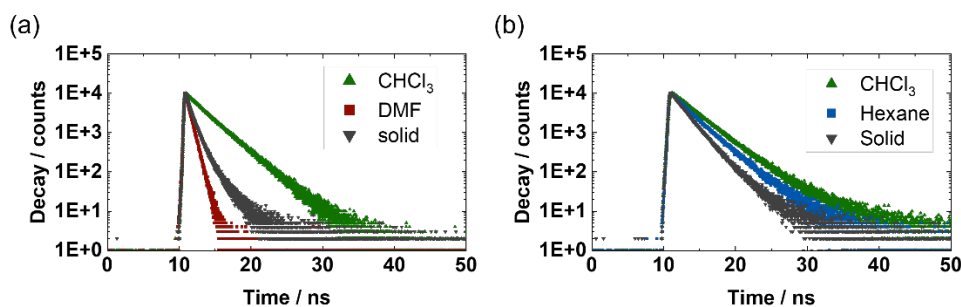


Figure S1. PL lifetime decay curves of (a) **PLB-TEG** and (b) **PLB-2DTD** in the solution and solid states.

Table S1. Photophysical properties of **PLB-R** in the solid states

Sample	$\lambda_{\text{PL}} / \text{nm}^a$	Φ_{PL}^b	τ / ns^c	$k_r / 10^8 \text{ s}^{-1}^d$	$k_{\text{nr}} / 10^8 \text{ s}^{-1}^d$
PLB-DD	567	0.33	1.2 (25.00%)	1.4	2.9
			2.7 (75.00%)		
PLB-TEG	568	0.07	0.35 (31.07%)	0.79	10
			0.96 (60.87%)		
			2.5 (8.06%)		
PLB-2DTD	562	0.20	1.4 (46.51%)	1.0	10
			2.5 (53.49%)		

^a Wavelength at emission maxima. Excited at λ_{abs} . ^b Absolute quantum yield determined by an integration sphere method. Excited at λ_{abs} . ^c Fluorescence lifetime determined by time-correlated single-photon counting. Excited with an LED laser at 375 nm. Fraction of component i , f_i , is shown in the parentheses. ^d k_r and k_{nr} were calculated with the following formula: $k_r = \Phi_{\text{PL}} / \langle \tau \rangle$; $k_{\text{nr}} = (1 - \Phi_{\text{PL}}) / \langle \tau \rangle$, where $\langle \tau \rangle = \sum f_i \tau_i$.

6. SEC Chart

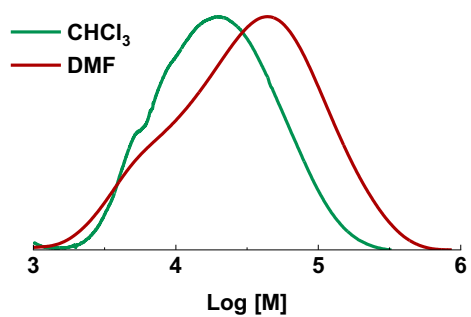


Figure S2. The differential molecular weight distribution of **PLB-TEG** in the chloroform and DMF solutions.

7. Supplementary References

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