Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Synthesis of Conjugated Polymers Containing Gallium Atoms and Evaluation of Conjugation through Four-Coordinate Gallium Atoms

Takuya Matsumoto[a], Yoshinobu Onishi[a], Kazuo Tanaka*[a], Hiroyuki Fueno[b], Kazuyoshi Tanaka[b] and Yoshiki Chujo*[a]

[a] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

[b] Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

General ^{1}H (400 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 and JNM-AL400 spectrometers. ^{1}H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard in $CDCl_3$, CD_2Cl_2 and C_6D_6. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE for atomic pressure chemical ionization (APCI) and electron spray ionization (ESI). Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. UV–vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and the absolute quantum yield was calculated by integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. X-ray crystallographic analysis was carried out by a Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with an imaging plate. A symmetry related absorption correction was carried out by using the program ABSCOR[1]. The analysis was carried out with direct methods (SHELX-97[2] or SIR97[3]) using Yadokari-XG[4]. The program ORTEP3[5] was used to generate the X-ray structural diagram. All reactions were performed under argon atmosphere.

Materials. All reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified using a two-column solid-state purification system (Glass Contour Solvent System, Joerg Meyer, Irvine, CA). 2,5-Didecyloxybenzene-1,4-diboronic acid bis(pinacol)ester[6], 2,5-diphenyl-1,4-didecyloxybenzene (**model 4**)[7], and dichloro[2,6-di-*t*-butyl-4-(*N,N*-dimethylaminomethyl)phenyl]gallane (**MamxGaCl$_2$**)[8] were prepared according to the literatures.

Synthesis of model 1. To a cold (−78 °C) solution of iodobenzene (1.6 g, 7.9 mmol) in Et_2O (40 mL), *n*-BuLi (1.6 M in hexane, 5.9 mL, 9.5 mmol) was added dropwise. The reaction mixture was stirred for 2 h and a cold (0 °C) solution of **MamxGaCl$_2$** (1.0 g, 3.2 room temperature and stirred for 24 h, yielding a pale yellow solution with white precipitate. The resulting solution was washed with water and brine, dried over Na_2SO_4, and then filtered. Evaporation provided the crude product. After purification by silica gel column chromatography (hexane : ethyl acetate = 30 : 1), recrystallization (chloroform/methanol) gave the product as a colorless solid (1.2 g, 83%). ^{1}H NMR (C_6D_6, δ, ppm): 1.41 (s, 9H), 1.48 (s, 9H), 1.76 (s, 6H), 3.25 (s, 2H), 7.03 (s, 1H), 7.29 (m, 6H), 7.73 (s, 1H), 7.91 (d, J = 1.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm): 31.5, 32.8, 34.6, 37.3,

46.8, 67.8, 119.2, 127.4, 138.0, 140.0, 143.5, 147.7, 149.7, 159.2. FTMS (ESI) m/z calcd $[M+H]^+$: 470.2333; found: 470.2326.

Synthesis of model 2. To a cold (−78 °C) solution of 5-iodo-*m*-xylene (0.67 g, 2.9 mmol) in Et_2O (15 mL), *n*-BuLi (1.6 M in hexane, 2.1 mL, 4.3 mmol) was added dropwise. The reaction mixture was stirred for 1.5 h and a cold (0 °C) solution of **MamxGaCl$_2$** (0.5 g, 1.6 mmol) in Et_2O (10 mL) was added dropwise. The resulting mixture was warmed up to room temperature and stirred for 24 h, yielding a dark pale yellow solution with white precipitate. The resulting solution was washed with water and brine, dried over Na_2SO_4, and then filtered. Evaporation provided the crude product. After purification by recrystallization (chloroform/methanol) gave the product as a colorless solid (0.33 g, 44%). ^{1}H NMR (C_6D_6, δ, ppm): 1.38 (s, 9H), 1.55 (s, 9H), 1.90 (s, 6H), 2.24 (s, 12H), 3.39 (s, 2H), 6.94 (s, 2H), 7.06 (s, 1H), 7.68 (s, 4H), 7.75 (s, 1H); ^{13}C NMR (C_6D_6, δ, ppm): 21.8, 31.9, 33.3, 34.9, 37.9, 46.6, 67.9, 119.5, 123.0, 129.6, 136.2, 136.5, 141.6, 144.2, 147.9, 150.0, 159.8. FTMS (APCI) m/z calcd $[M+H]^+$: 526.2959; found: 526.2949.

Synthesis of monomer. To a cold (−78 °C) solution of *p*-bromoiodobenzene (5.4 g, 19 mmol) in Et_2O (75 mL), *n*-BuLi (1.6 M in hexane, 14 mL, 23 mmol) was added dropwise. The reaction mixture was stirred for 2 h and a cold (0 °C) solution of **MamxGaCl$_2$** (2.4 g, 7.6 mmol) in Et_2O (40 mL) was added dropwise. The resulting mixture was warmed up to room temperature and stirred for 18 h, yielding a pale yellow solution with white precipitate. The resulting solution was washed with water and brine, dried over Na_2SO_4, and then filtered. Evaporation provided the crude product. After purification by silica gel column chromatography (hexane : ethyl acetate = 40 : 1), recrystallization from chloroform/methanol gave the product as a colorless solid (2.51g, 53%). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.25 (s, 9H), 1.36 (s, 9H), 2.30 (s, 6H), 3.69 (s, 2H), 6.98 (s, 1H), 7.44 (d, J = 8.0 Hz, 4H), 7.48 (s, 1H), 7.55 (d, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm): 31.9, 33.1, 35.0, 37.6, 47.2, 68.1, 119.7, 122.6, 122.8, 130.8, 138.9, 139.6, 143.5, 145.9, 150.5, 159.4. FTMS (APCI) m/z calcd $[M+H]^+$: 660.0153; found: 660.0179.

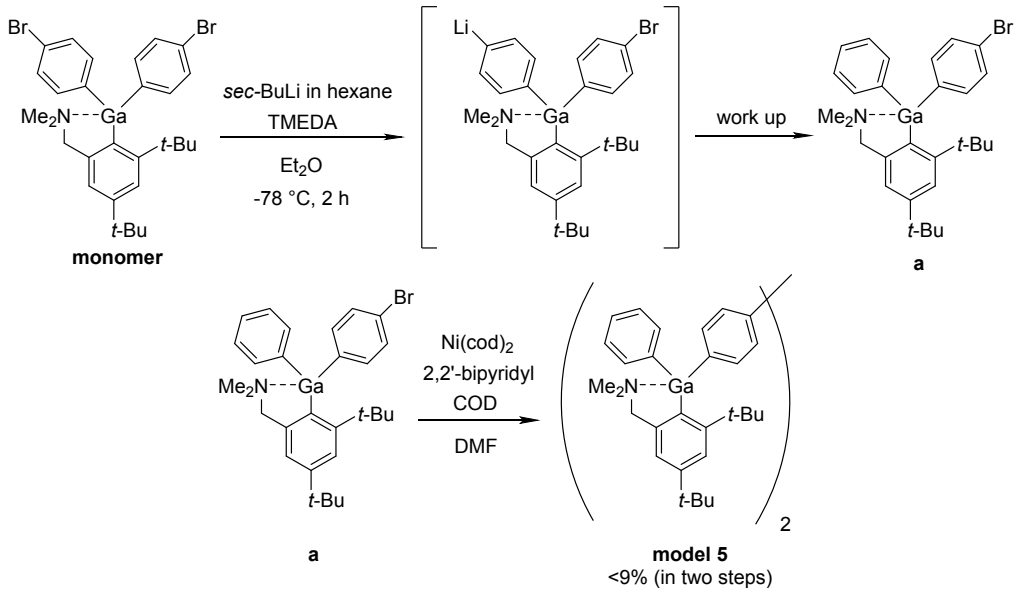
Synthesis of polymer 1. A mixture of 2,2'-bipyridyl (0.11 g, 0.36 mmol), $Ni(COD)_2$ (0.20 g, 0.36 mmol) and 1,5-cyclooctadiene (0.088 ml, 0.36 mmol) in 2 mL of DMF was stirred at 80 °C for 2 h, and then a solution of **monomer** (0.38 g, 0.6 mmol) in 2 mL of DMF was added into the mixture. After the mixture was stirred for 22 h, the resulting solution was washed with water and brine and dried over Na_2SO_4. Subsequently, three

times reprecipitation into methanol gave **polymer 1** as a colorless powder (33 mg, 12%). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.37 (br, 9H), 1.38 (br, 9H), 2.35 (br, 6H), 3.74 (br, 2H), 6.99 (br, 1H), 7.50 (br, 1H), 7.61 (br, 4H), 7.83 (br, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm): 31.4, 31.5, 32.6, 32.9, 34.6, 37.4, 46.9, 67.9, 119.3, 122.3, 125.9, 127.0, 128.6, 138.4, 140.2, 143.6, 146.2, 159.3.

Synthesis of polymer 2. The solution containing **monomer** (190 mg, 0.3 mmol), 2,5-didecyloxybenzene-1,4-diboronic acid bis(pinacol)ester (190 mg, 0.3 mmol), chloro[(tri-*tert*-butylphosphine)-2-(aminobiphenyl)]palladium(II) (7.7 mg, 15 μmol) and Cs_2CO_3 (590 mg, 1.8 mmol) in toluene (2 mL) and water (0.7 mL) was refluxed for 13 h and extracted with $CHCl_3$. The organic layer was washed with distilled water and brine. After drying over Na_2SO_4, three times reprecipitation into methanol gave **polymer 2** as a colorless powder (130 mg, 50%). ^{1}H NMR (CD_2Cl_2, δ, ppm): 0.84 (br, 6H), 1.17–1.43 (br, 46H), 1.71 (br, 4H), 2.41 (br, 6H), 3.80 (br, 2H), 3.96 (br, 4H), 7.04 (br, 2H), 7.07 (br, 1H), 7.54 (br, 1H), 7.56–7.61 (br, 4H), 7.78–7.83 (br, 4H); ^{13}C NMR (CD_2Cl_2, δ, ppm): 14.3, 23.1, 25.0, 26.5, 29.7, 29.8, 29.8, 29.9, 30.0, 31.7, 32.3, 32.8, 32.9, 33.1, 34.9, 37.7, 47.2, 68.1, 69.8, 116.4, 119.9, 122.8, 128.3, 128.9, 129.9, 131.1, 137.9, 138.0, 144.3, 146.6, 150.7, 159.6.

Synthesis of model 3. The solution containing **monomer** (680 mg, 1.1 mmol), phenylboronic acid pinacol ester (480 mg, 2.4 mmol), chloro[(tri-*tert*-butylphosphine)-2-(aminobiphenyl)]palladium(II) (28 mg, 54 μmol) and Cs_2CO_3 (2.1 g, 6.5 mmol) in toluene (7 mL) and water (2.5 mL) was refluxed for 13 h and extracted with $CHCl_3$. The organic layer was washed with distilled water and brine. After filtration, evaporation provided the crude product. After purification by basic alumina column chromatography (hexane : ethyl acetate = 30 : 1), recrystallization from chloroform/methanol gave the product as a colorless solid (430 mg, 63%). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.34 (s, 9H), 1.38 (s, 9H), 2.36 (s, 6H), 3.75 (s, 2H), 7.00 (d, J = 1.7 Hz, 1H), 7.31 (t, J = 7.4 Hz, 2H), 7.42 (dd, J = 7.6 Hz, 7.8 Hz, 4H), 7.51 (d, J = 1.7 Hz, 1H), 7.57 (d, J = 8.1 Hz, 4H), 7.63 (d, J = 7.1 Hz, 4H), 7.84 (d, J = 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, δ, ppm): 31.6, 32.9, 34.6, 37.4, 46.9, 67.8, 119.3, 122.6, 122.3, 126.0, 126.9, 127.0, 128.7, 138.5, 139.9, 139.9, 141.6, 143.5, 146.5, 159.3. FTMS (APCI) m/z calcd $[M+H]^+$: 622.2959; found: 622.2947.

Scheme S1. Synthsis of **model 5**



Synthesis of model 5.

To a cold (−78 ºC) solution of monomer (1.3 g, 2.1 mmol) N,N,N',N'-tetramethylenediamine (TMEDA, 0.43 mL, 2.9 mmol) in Et_2O (20 mL), *sec*-BuLi (1.1 M in hexane, 2.7 mL, 2.9 mmol) was added slowly. The reaction mixture was stirred for 2 h and quenched with water. The resulting solution was washed with water and brine, dried over Na_2SO_4, and then filtered. Evaporation provided the crude product (1.1 g). The crude product **a** was used for the next reaction without more purification. The mixture of 2,2'-bipyridyl (0.11 g, 0.67 mmol), $Ni(COD)_2$ (0.19 g, 0.67 mmol) and 1,5-cyclooctadiene (0.082 ml, 0.67 mmol) in 2 ml of DMF was stirred at 80 ºC for 1 h, and then a solution of **a** (0.61 g, 1.1 mmol) in 3 ml of DMF was added into the mixture. After the mixture was stirred for 15 h, the resulting solution was washed with water and brine, dried over Na_2SO_4, and then filtered. Evaporation provided the yellow oil. After purification by high performance liquid chromatography (HPLC) gave the product **model 5** as a colorless solid (0.89 mg, 9% in two steps). ^{1}H NMR ($CDCl_3$, δ, ppm): 1.24-1.45 (m, 36H), 2.25-2.38 (m, 12H), 3.71 (s, 4H), 6.98 (s, 2H), 7.26-7.34 (m, 6H), 7.49 (s, 2H), 7.59 (d, J = 7.7 Hz, 4H), 7.74-7.82 (m, 8H); ^{13}C NMR ($CDCl_3$, δ, ppm): 31.6, 32.9, 34.6, 37.3, 46.8, 46.8, 67.9, 119.2, 122.3, 125.8, 127.3, 127.4, 138.0, 138.4, 140.1, 140.2, 143.5, 146.1, 147.8, 149.8, 159.3. FTMS (APCI) m/z calcd $[M+H]^+$: 937.4436; found: 937.4412.

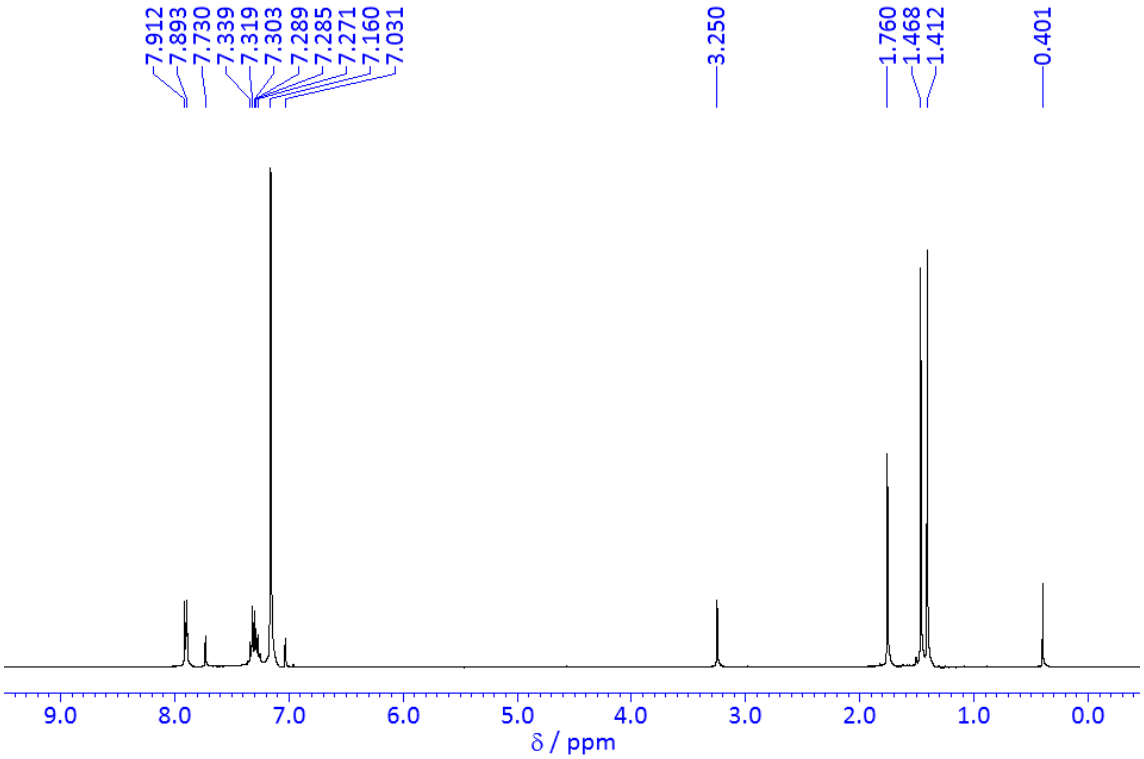


Figure S1. ^{1}H NMR spectrum of **model 1** in C_6D_6.

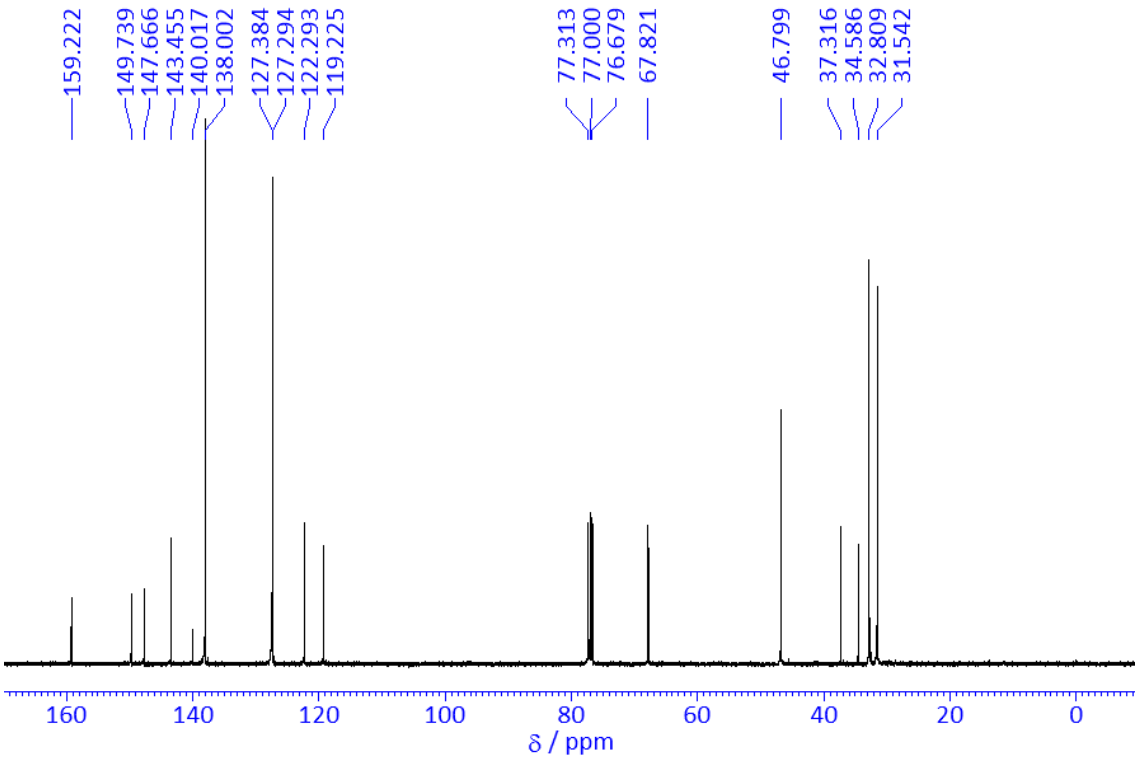


Figure S2. ^{13}C NMR spectrum of **model 1** in $CDCl_3$.

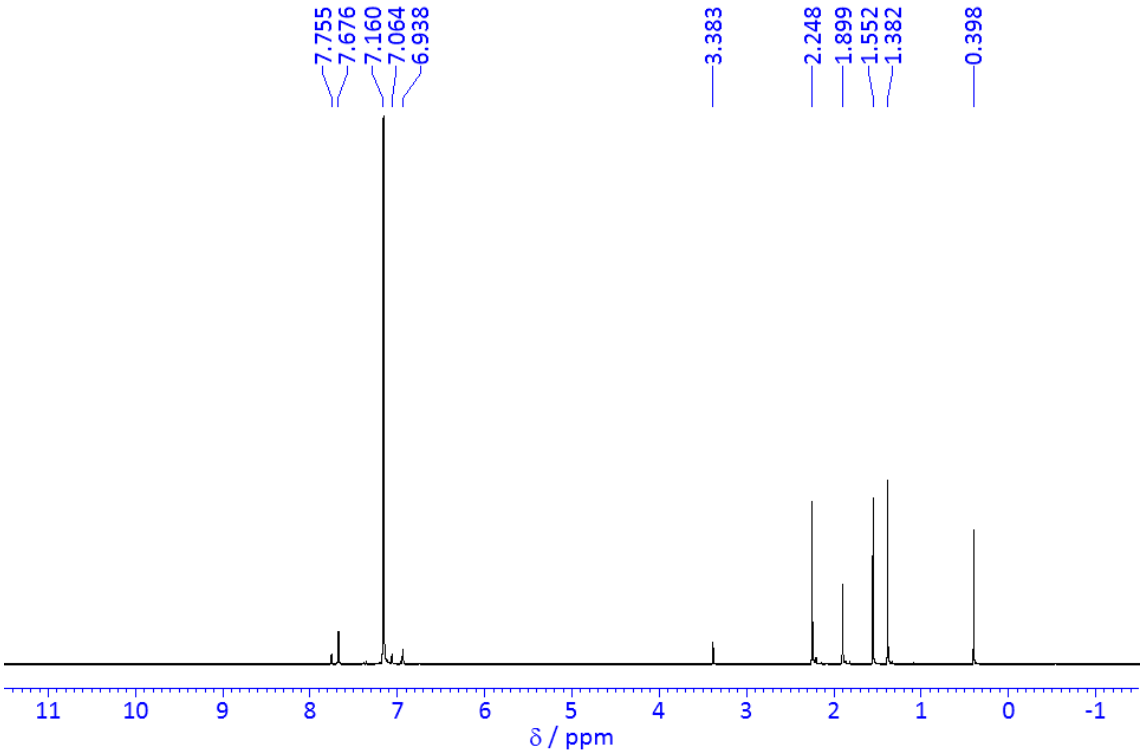


Figure S3. ^{1}H NMR spectrum of **model 2** in C_6D_6.

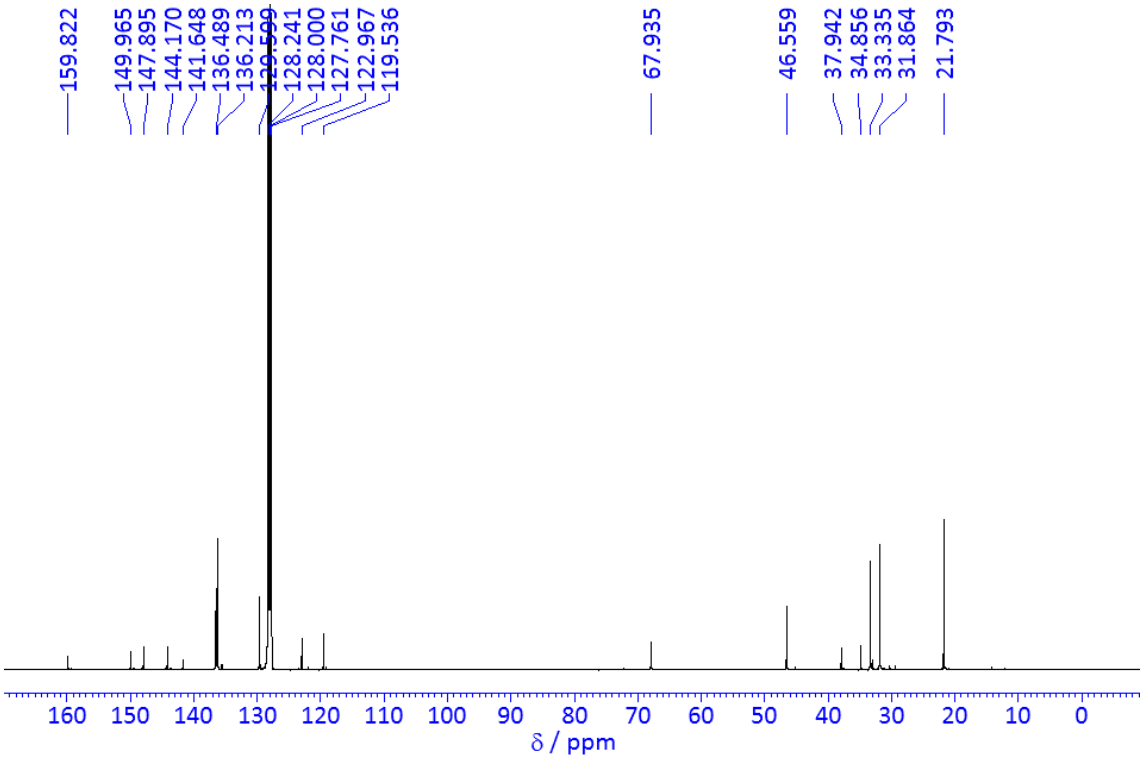


Figure S4. ^{13}C NMR spectrum of **model 2** in C_6D_6.

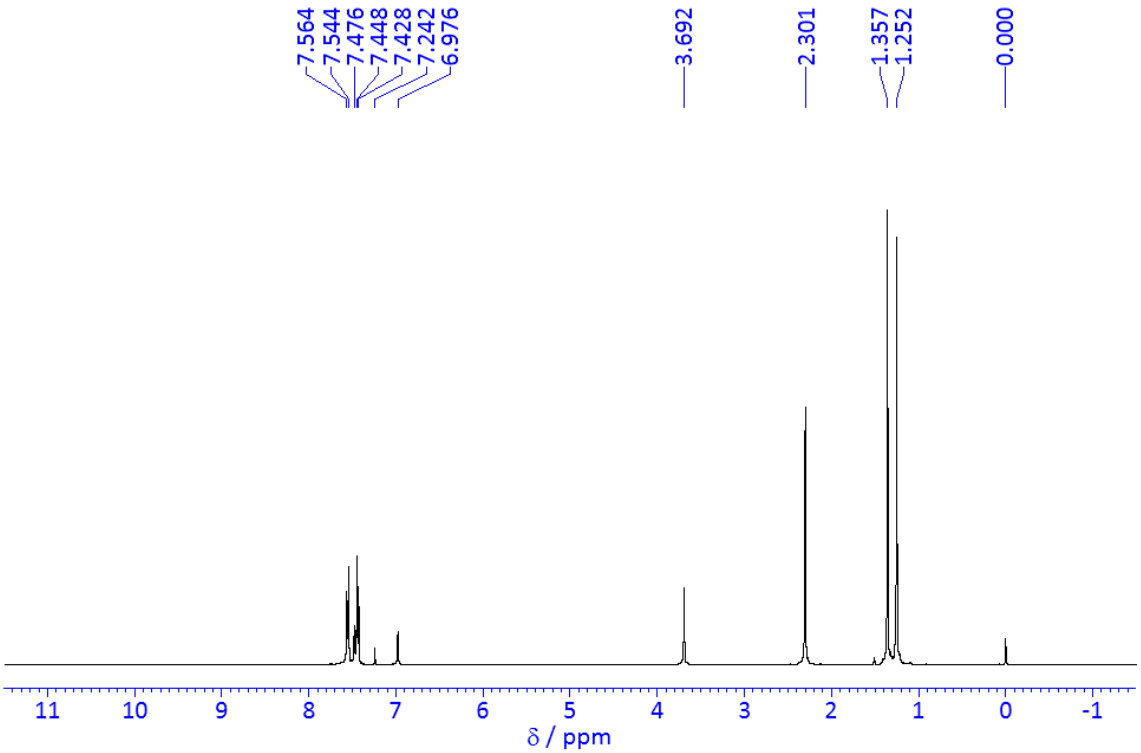


Figure S5. ^{1}H NMR spectrum of **monomer** in $CDCl_3$.

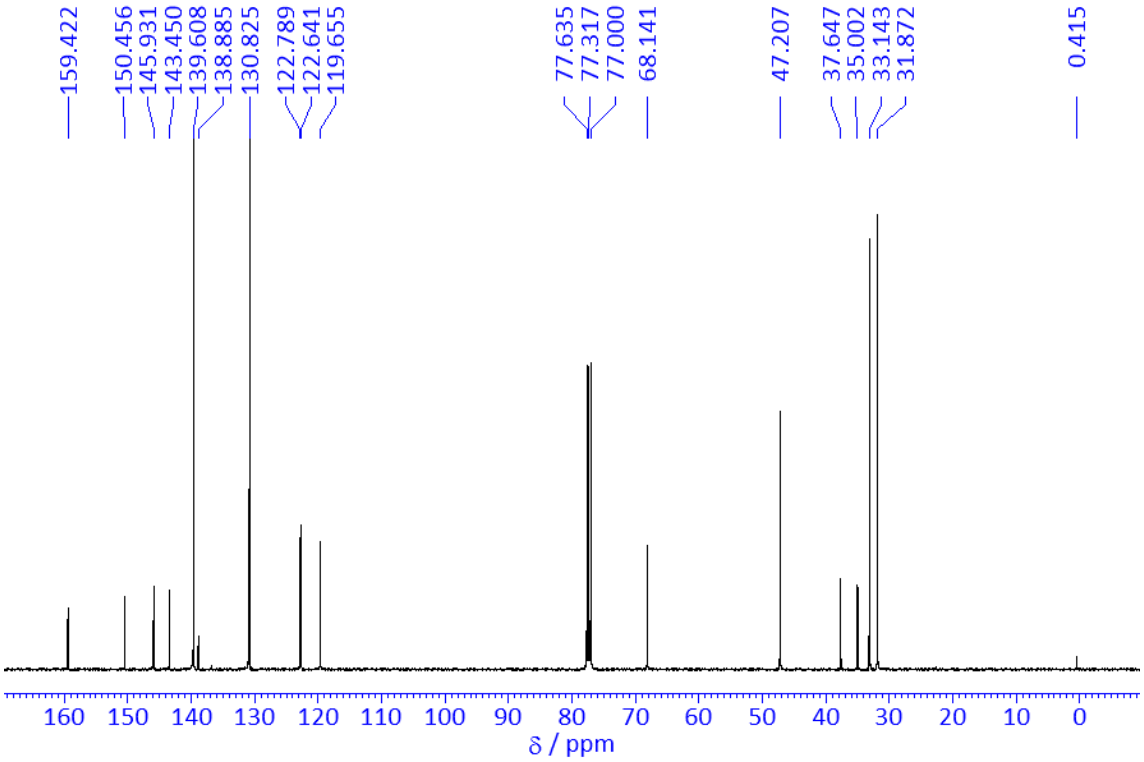


Figure S6. ^{13}C NMR spectrum of **monomer** in $CDCl_3$.

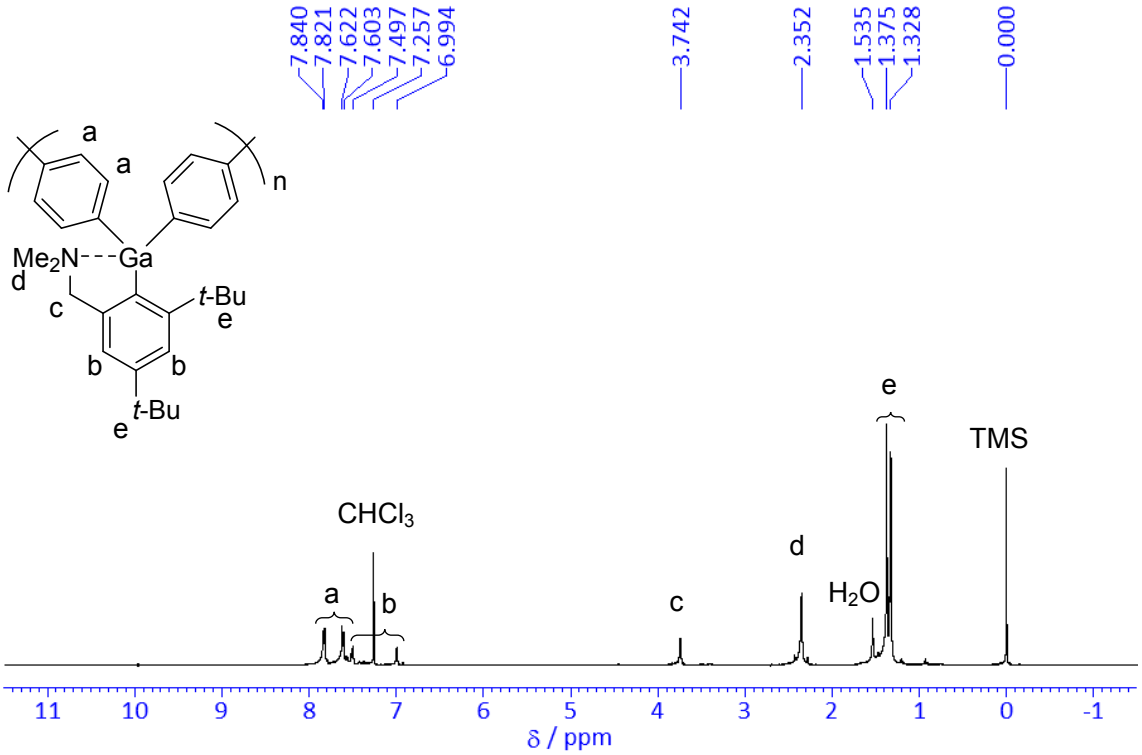


Figure S7. ^{1}H NMR spectrum of **polymer 1** in $CDCl_3$.

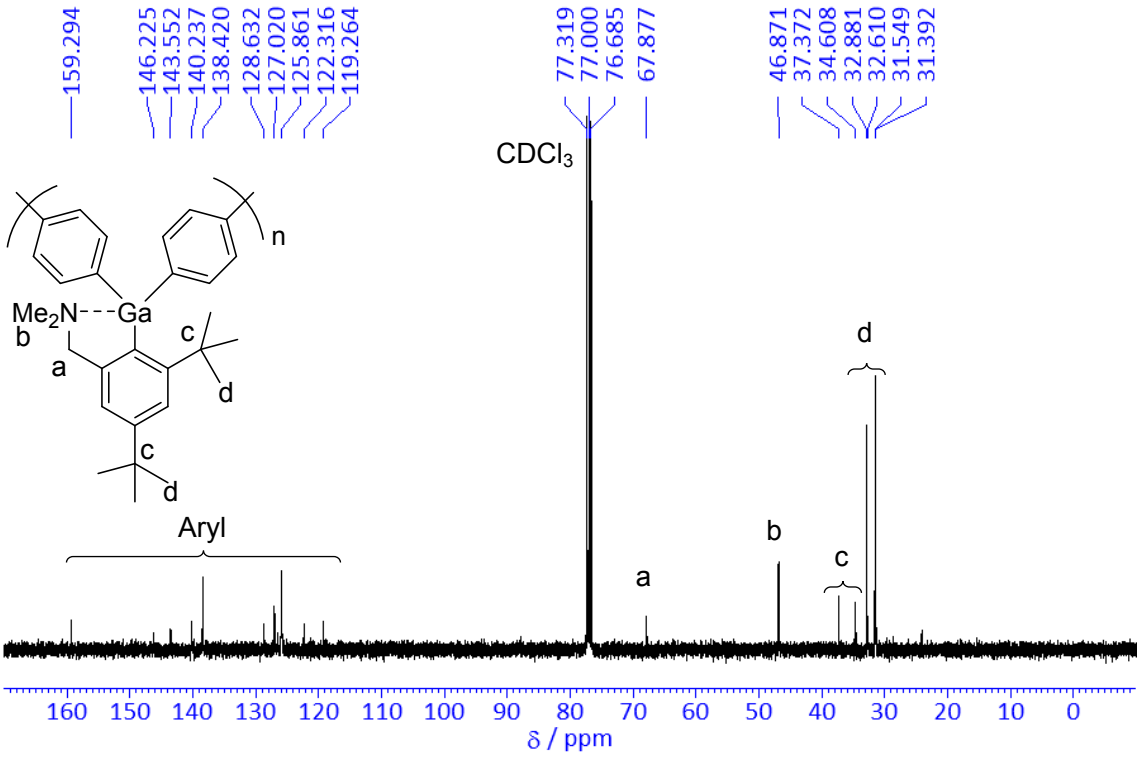


Figure S8. ^{13}C NMR spectrum of **polymer 1** in $CDCl_3$.

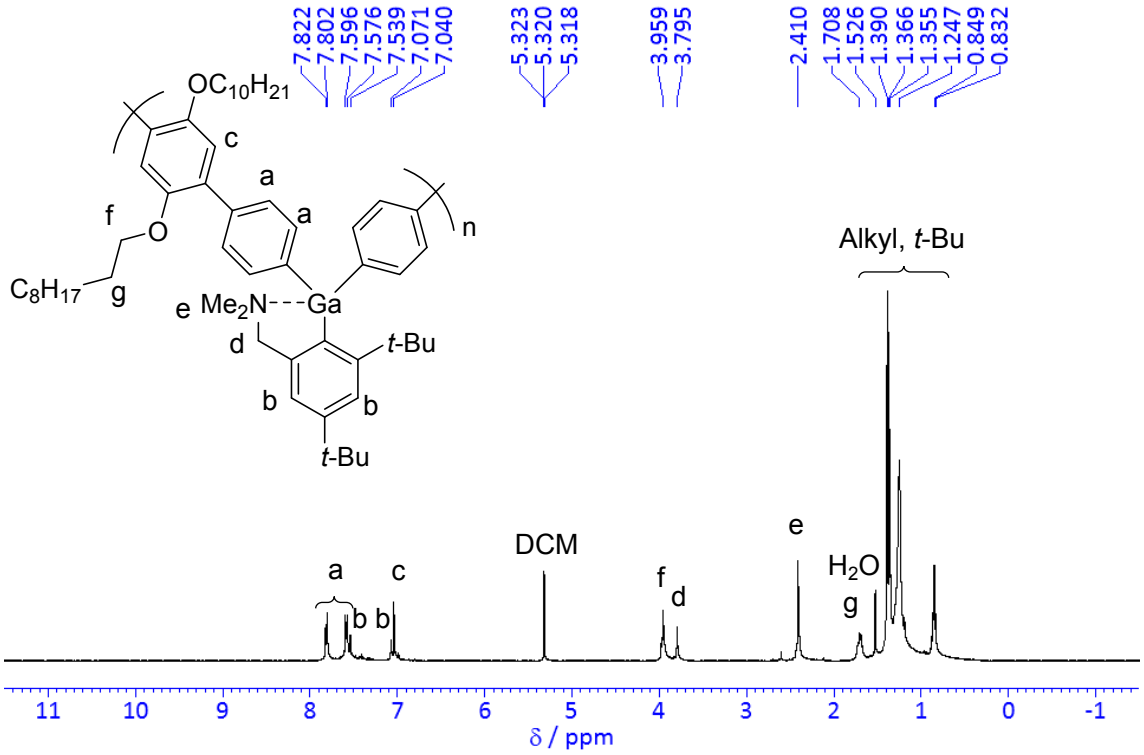


Figure S9. ^{1}H NMR spectrum of **polymer 2** in CD_2Cl_2.

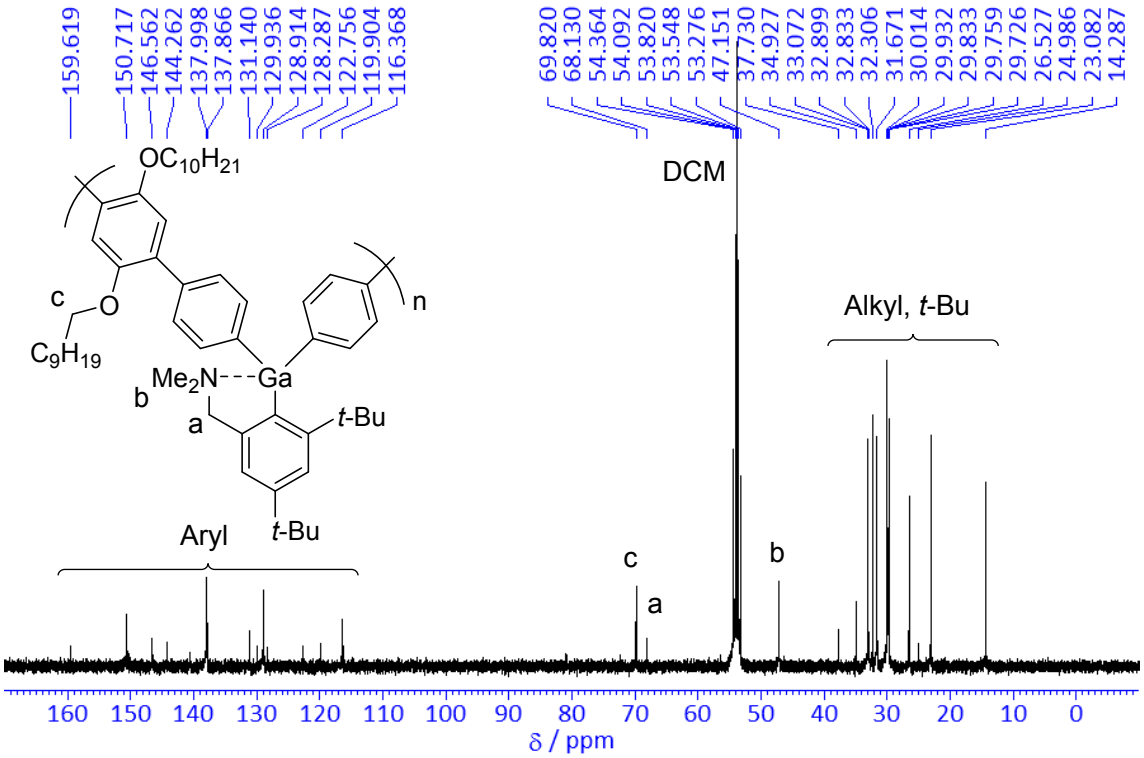


Figure S10. ^{13}C NMR spectrum of **polymer 2** in CD_2Cl_2.

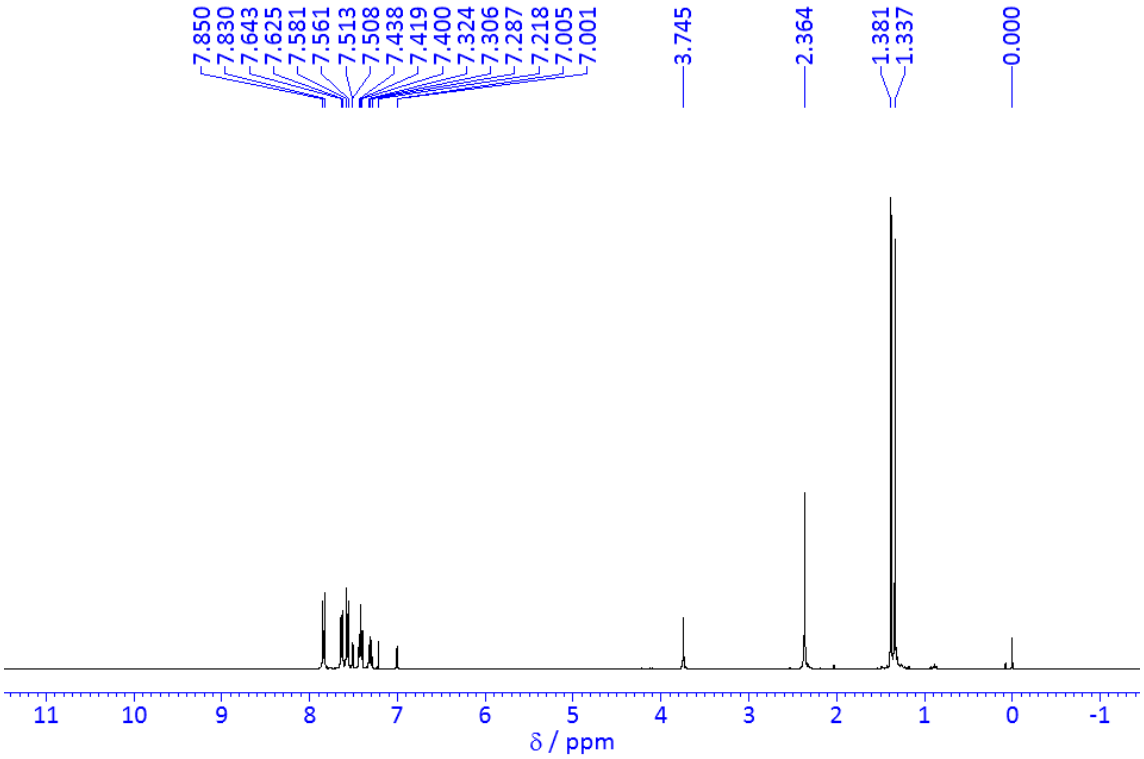


Figure S11. ^{1}H NMR spectrum of **model 3** in $CDCl_3$.

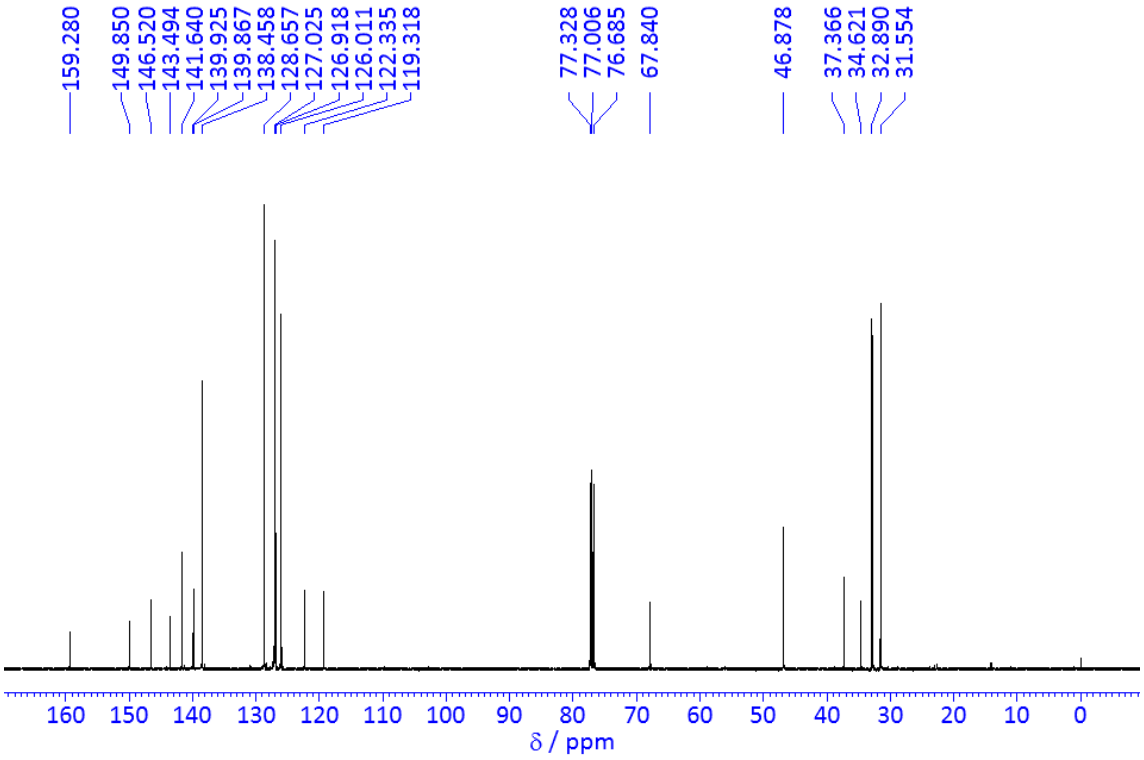


Figure S12. ^{13}C NMR spectrum of **model 3** in $CDCl_3$.

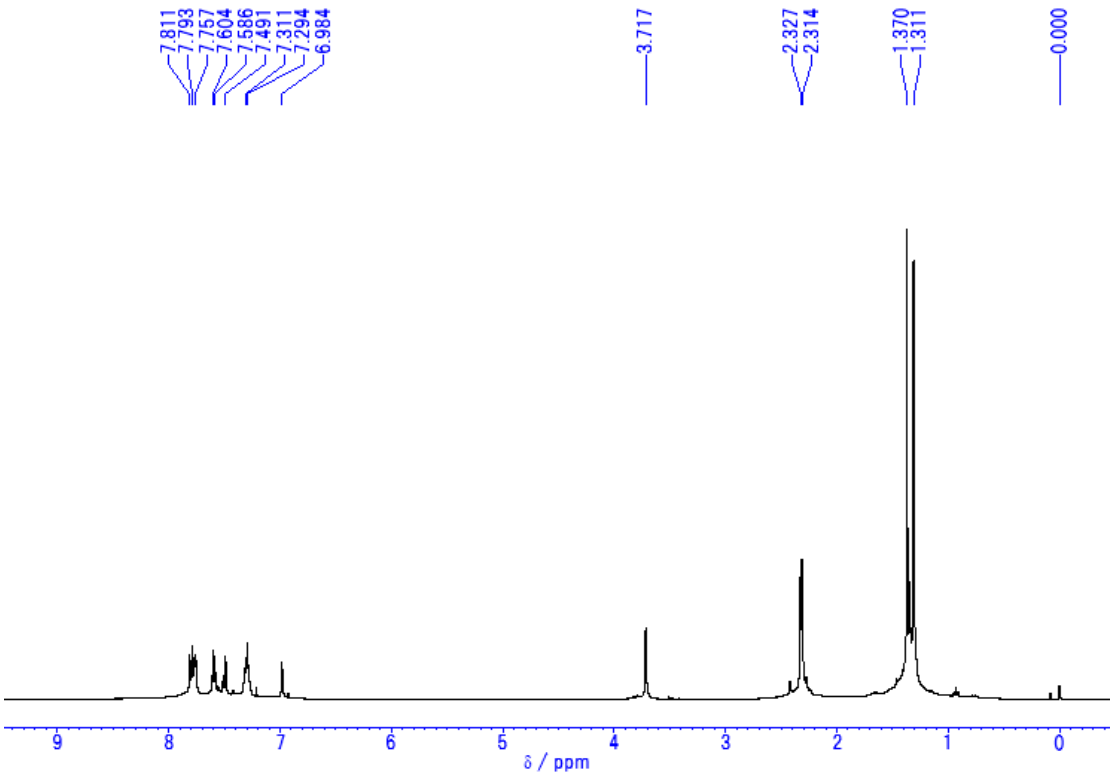


Figure S13. ^{1}H NMR spectrum of **model 5** in $CDCl_3$.

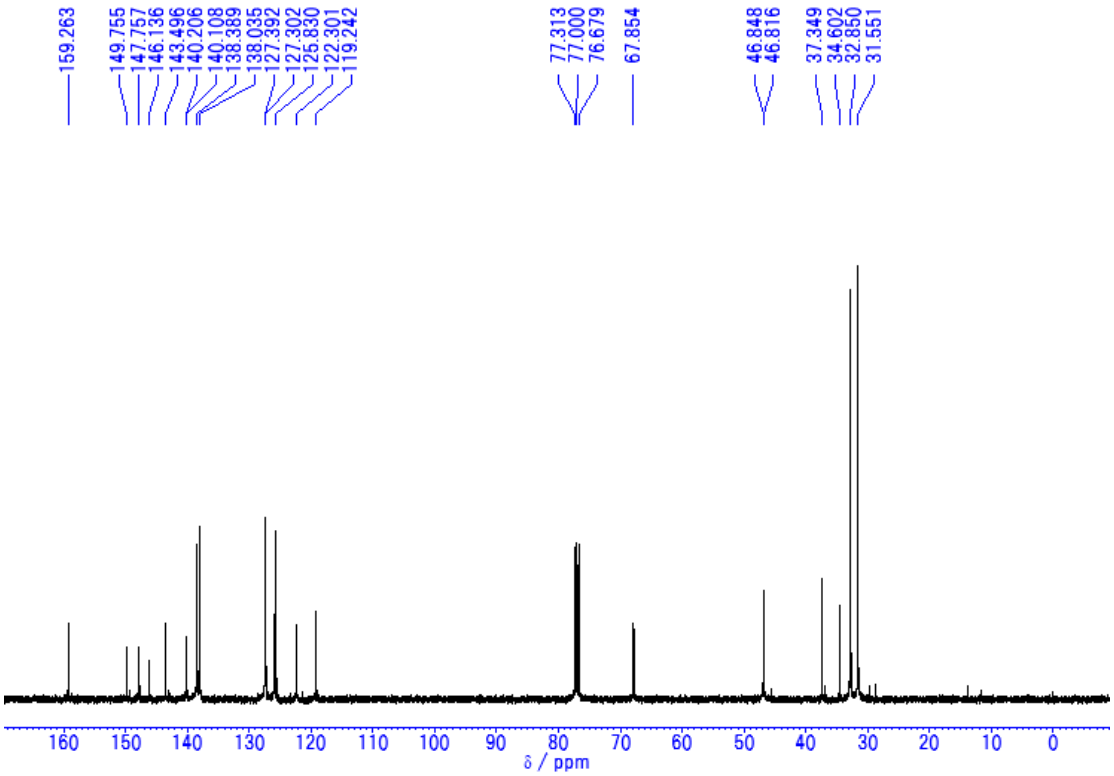


Figure S14. ^{13}C NMR spectrum of **model 5** in $CDCl_3$.

X-ray Crystal Structure Analysis

Intensity data were collected on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo *K*α radiation at –180 °C. The structures were solved by direct method (SIR97)[9] and refined by full-matrix least-squares procedures based on F^2 (SHELX-97).[10]

Table S1. Crystallographic data of **model 2**

Empirical formula	$C_{33}H_{46}GaN$
Formula weight	526.43
Temperature (K)	93(2)
Wavelength (Å)	0.71075
Crystal system, space group	monoclinic, *P21/c*
Unit cell dimensions	a = 8.0037(11)
	b = 42.296(5)
	c = 9.1578(11)
	α = 90
	β = 98.422(7)
	γ = 90
V (Å^3)	3066.7(7)
Z, calculated density (Mg m^{-3})	4, 1.140
Absorption coefficient	0.917
F(000)	1128
Crystal size (mm)	0.20 × 0.30 × 0.40
θ range for data collection	3.20–27.49
Limiting indices	$-10\le h\le 10$, $-54\le k\le 54$, $-11\le l\le 11$
Reflections collected (unique)	29745/7025 [R(int) = 0.0894]
Completeness to theta = 27.93	0.998
Max. and min. transmission	0.838 and 0.711
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0601 wR_2 = 0.1407
R indices (all data)	R_1 = 0.1106, wR_2 = 0.1693

[a] $R_1 = \Sigma(|F_0|-|F_c|)/\Sigma|F_0|$. w$R_2 = [\Sigma w(F^2_0-F^2_c)^2/\ \Sigma w(F^2_0)^2]^{1/2}$. $w = 1/[\sigma^2(F^2_0)+[(ap)^2+bp]]$, where $p = [\max(F^2_0,0)+2F^2_c]/3$.

UV−vis absorption and photoluminescence (PL) data

Table S2. UV−vis absorption and PL data for biphenyl, **model 3** and **polymer 1**

	$\lambda_{max,\ abs}$ (nm)[a]	$\varepsilon_{abs,\ max,\ abs}$ ($M^{-1}cm^{-1}$)	$\lambda_{onset,\ abs}$ (nm)	$\lambda_{max,\ FL}$ (nm)[b]	Φ_F[c]	$\tau_{1/2}$ (ns)
biphenyl	250	14,900	280	314	<0.01	—
model 3	263	47,500	294	319	0.01	0.017 (98%) (χ^2 = 1.14)
model 5	269	41,700	303	322	0.04	0.014 (100%) (χ^2 = 1.08)
polymer 1	275	38,300	306	378	0.32	0.014 (100%) (χ^2 = 0.96)
model 1	241	6,990	251	—	—	—
monomer	242	14,170	251	—	—	—

[a] Absorption maxima: 1.0×10^{-5} M in $CHCl_3$ solution. [b] Fluorescence maxima excited at $\lambda_{max,\ abs}$: 1.0×10^{-5} M in $CHCl_3$ solution. [c] Relative quantum yield by using naphthalene[11] as a standard.

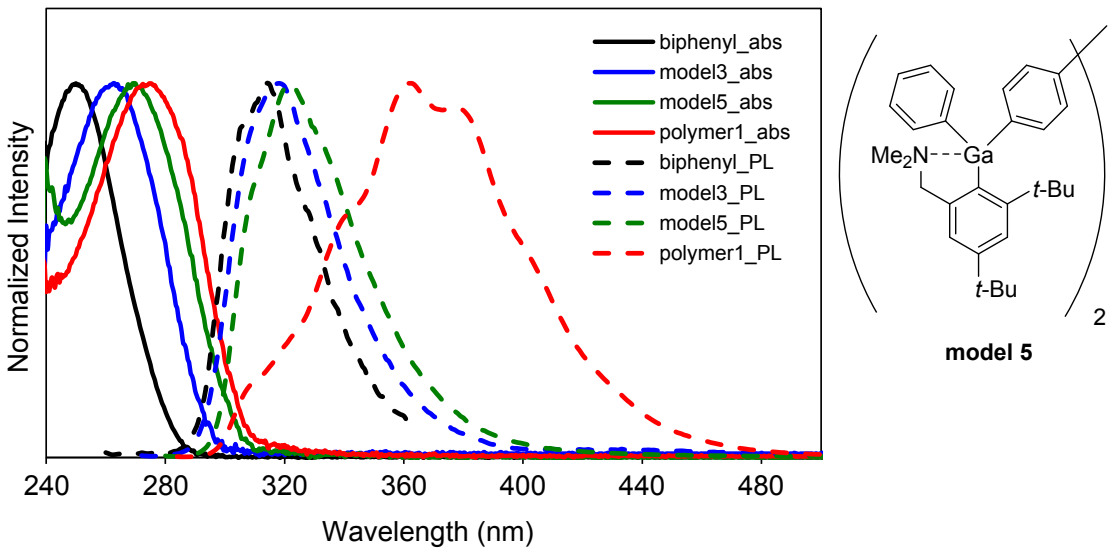


Figure S15. UV−vis absorption (solid lines) and PL (dashed lines, excited at $\lambda_{max,\ abs}$) spectra of biphenyl (black), **model 3** (blue), **model 5** (green) and **polymer 1** (red) in $CHCl_3$ solution (1.0×10^{-5} M).

Table S3. UV−vis absorption and PL data for **model 4** and **polymer 2**

	$\lambda_{max,\ abs}$ (nm)[a]	$\varepsilon_{max,\ abs}$ ($M^{-1}cm^{-1}$)	$\lambda_{onset,\ abs}$ (nm)	$\lambda_{max,\ FL}$ (nm)[b]	Φ_F[c]	$\tau_{1/2}$ (ns)
model 4	266, 318	17,800, 10,900	354	384	0.16	0.83 (100%) (χ^2 = 1.16)
polymer 2	277, 325	23,800, 16,500	360	392	0.23	0.62 (100%) (χ^2 = 0.91)

[a] Absorption maxima: 1.0×10^{-5} M in $CHCl_3$ solution. [b] Fluorescence maxima excited at $\lambda_{max,\ abs}$: 1.0×10^{-5} M in $CHCl_3$ solution. [c] Absolute quantum yield.

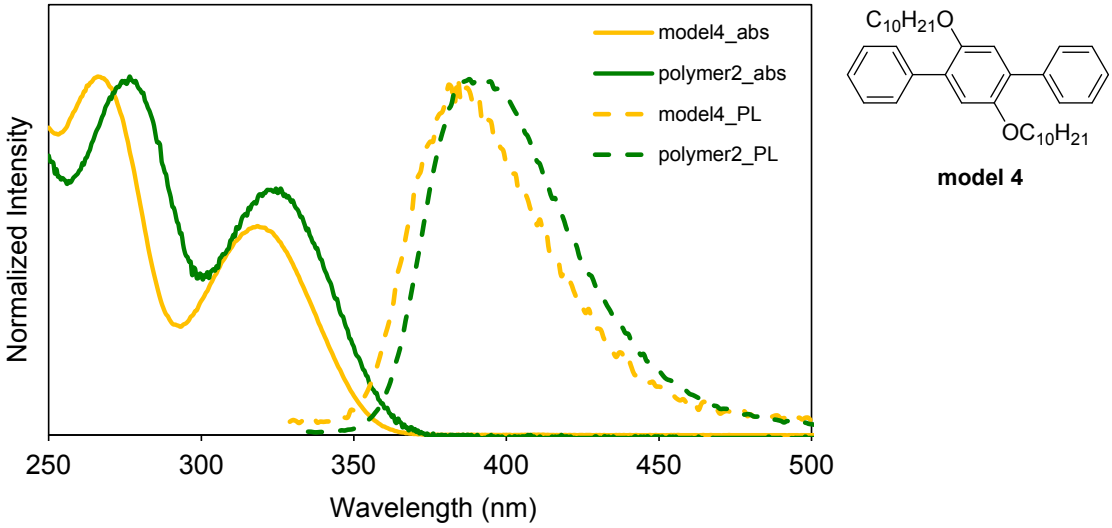


Figure S16. UV−vis absorption (solid lines) and PL (dashed lines, excited at $\lambda_{max,\ abs}$) spectra of **model 4** (yellow) and **polymer 2** (green) in $CHCl_3$ soluion (1.0×10^{-5} M).

Density functional theory (DFT) calculation by Gaussian 09 program[12]

The optimized structure of **model 3** was obtained by DFT calculation at the B3LYP/6-31G(d,p) level. TD-DFT calculation was carried out at the B3LYP/6-31G(d,p) level for the electronic transitions.

Table S4. Cartesian coordinates of the optimized structure of **model 3**

Center Symbol	Coordinates (Angstroms) X	Y	Z
Ga	−0.073471	0.009037	−0.377846
C	−1.924165	−0.661552	−0.184221
C	1.436380	−1.259108	−0.215348
C	−2.940563	0.103277	0.411956
C	−4.247095	−0.365425	0.533927
C	−4.604198	−1.642468	0.070849
C	−3.599007	−2.418677	−0.527619
C	−2.295985	−1.936507	−0.646128
C	1.298318	−2.645011	−0.032891
C	2.400565	−3.487488	0.102413
C	3.709213	−2.979346	0.063132
C	3.862259	−1.593203	−0.103401
C	2.751832	−0.760967	−0.230820
C	0.921250	1.633809	−2.500518
C	0.434520	1.906911	−0.054827
C	0.485589	2.708426	1.104488
C	0.805229	4.070594	0.974802
C	1.105931	4.689665	−0.243851
C	1.110538	3.874239	−1.379421
C	0.783442	2.522535	−1.276105
C	−5.993148	−2.150813	0.201654
C	4.885839	−3.874131	0.202883
C	−7.095892	−1.293737	0.045410
C	−8.399565	−1.771798	0.166626
C	−8.631649	−3.119486	0.446201
C	−7.546943	−3.983623	0.604290
C	−6.243591	−3.504533	0.484293
C	4.888395	−5.159214	−0.366279
C	5.991213	−6.001253	−0.234175
C	7.119744	−5.577445	0.469455
C	7.133404	−4.303510	1.039811
C	6.029570	−3.462621	0.908421
N	−0.079717	0.535354	−2.466027
C	0.303481	−0.596381	−3.328619
C	−1.410161	1.050464	−2.855880
C	1.429194	6.194714	−0.288562
C	0.223117	6.999022	0.251405
C	1.728725	6.685050	−1.717804

C	2.670374	6.485480	0.588059
C	0.248284	2.183937	2.544111
C	1.471920	2.536551	3.427053
C	−1.014897	2.851588	3.138234
C	0.072454	0.656636	2.626737
H	−2.718458	1.100666	0.785593
H	−4.997346	0.251018	1.021755
H	−3.849010	−3.398835	−0.924499
H	−1.561245	−2.571264	−1.137622
H	0.306047	−3.083797	0.033417
H	2.248666	−4.549970	0.272322
H	4.862308	−1.170512	−0.150686
H	2.919211	0.309079	−0.340960
H	1.911299	1.162068	−2.499568
H	0.832945	2.203185	−3.437019
H	0.818743	4.683556	1.870063
H	1.363750	4.282907	−2.352600
H	−6.927890	−0.248914	−0.198023
H	−9.236028	−1.091423	0.033711
H	−9.647316	−3.492364	0.540309
H	−7.715170	−5.032652	0.831092
H	−5.407065	−4.180012	0.636214
H	4.026006	−5.489727	−0.937451
H	5.971941	−6.987608	−0.689198
H	7.979312	−6.233181	0.572713
H	8.002536	−3.966060	1.597488
H	6.040626	−2.484690	1.380165
H	0.385396	−0.295346	−4.381899
H	1.251387	−1.017407	−2.990083
H	−0.453233	−1.380654	−3.246378
H	−1.674882	1.894437	−2.216872
H	−1.407256	1.379767	−3.903960
H	−2.160854	0.272653	−2.715758
H	−0.018211	6.726652	1.282804
H	0.440297	8.073154	0.232476
H	−0.669546	6.822411	−0.357586
H	1.945102	7.758154	−1.702161
H	2.599691	6.179905	−2.148074
H	0.877302	6.529522	−2.388518
H	2.507941	6.199506	1.631180
H	2.909616	7.554948	0.568811
H	3.544099	5.935155	0.223896
H	1.638875	3.614295	3.502261
H	2.383421	2.084115	3.023011
H	1.325887	2.154273	4.443536
H	−0.925136	3.941825	3.165423
H	−1.186641	2.504700	4.163643
H	−1.903922	2.607044	2.547585

H	−0.817920	0.305154	2.098722
H	0.948661	0.125686	2.242858
H	−0.051827	0.363338	3.674823

Table S5. TD-DFT calculation result of **model 3**

Transition Energy (Wave Length)	Assignment with Contribution	Oscillator Strength *f*
4.668 eV (266 nm)	HOMO–>LUMO (90.32%) HOMO−2–>LUMO (9.68%)	0.4584
4.8207 eV (257 nm)	HOMO−1–>LUMO (45.05%) HOMO–>LUMO+1 (31.62%) HOMO−2–>LUMO (17.87%) HOMO–>LUMO (3.29%) HOMO−2–>LUMO+1 (2.17%)	0.0473
4.850 eV (256 nm)	HOMO−2–>LUMO (62.40%) HOMO−1–>LUMO (28.50%) HOMO–>LUMO (5.21%) HOMO−1–>LUMO+1 (3.90%)	0.1906
4.907 eV(253 nm)	HOMO−5–>LUMO (33.67%) HOMO−1–>LUMO+2 (25.07%) HOMO−5–>LUMO+1 (9.76%) HOMO–>LUMO+2 (9.71%) HOMO−1–>LUMO+3 (7.63%) HOMO−4–>LUMO (4.56%) HOMO−1–>LUMO+5 (4.25%) HOMO–>LUMO+4 (2.95%) HOMO−2–>LUMO (2.41%)	0.0169
4.915 eV(252 nm)	HOMO−4–>LUMO (25.30%) HOMO–>LUMO+4 (21.99%) HOMO−4–>LUMO+1 (18.37%) HOMO–>LUMO+7 (12.32%) HOMO−5–>LUMO (5.82%) HOMO−2–>LUMO (5.73%) HOMO−1–>LUMO+2 (4.62%) HOMO−1–>LUMO+4 (3.18%) HOMO–>LUMO+6 (2.56%)	0.0153

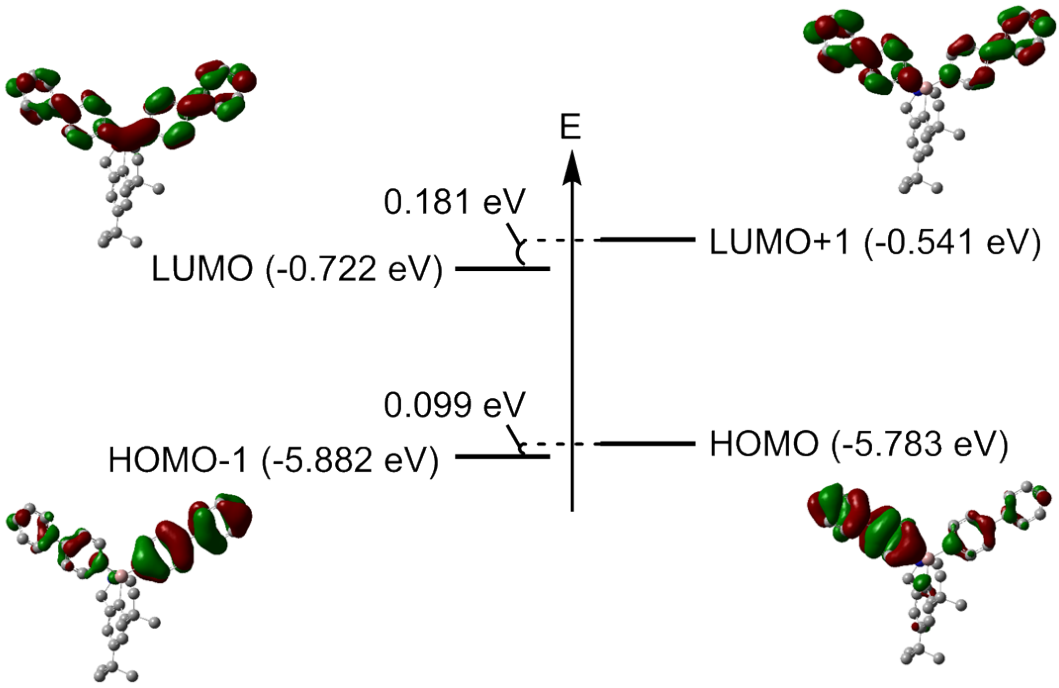


Figure S17. Energy levels and patterns of the selected MOs of **model 3**.

Density functional theory (DFT) calculation by Crystal 09 program[13]

The optimized structure of **polymer 1** was obtained by crystal orbital calculation at the B3LYP/6-31G(d,p) level.

Table S6. Cartesian coordinates of the optimized structure of **polymer 1**

Center Symbol	Coordinates (Angstroms)		
	X	Y	Z
Ga	4.833343	2.794773	−0.089707
C	6.557536	1.772006	−0.148058
C	3.109503	1.771408	−0.022574
C	7.715216	2.272676	−0.771565
C	8.929159	1.586239	−0.747237
C	9.054514	0.354252	−0.081952
C	7.909299	−0.155572	0.552270
C	6.698785	0.537579	0.514339
C	3.042943	0.366123	−0.031689
C	1.828582	−0.319743	−0.001998
C	0.606590	0.372721	0.046120
C	0.656865	1.777455	0.049384
C	1.876924	2.452159	0.009283
C	4.275224	4.953403	1.768961
C	4.706962	4.713003	−0.703157
C	4.803559	5.321166	−1.975715
C	4.820979	6.724777	−2.059364
C	4.730284	7.573768	−0.949987
C	4.573250	6.963778	0.298324
C	4.550319	5.571729	0.407572
C	−0.687953	−0.354686	0.081456
C	−0.813255	−1.586742	0.746628
C	−2.027156	−2.273245	0.770929
C	−3.184943	−1.772491	0.147665
C	−3.043784	−0.537936	−0.514506
C	−1.833243	0.155190	−0.552587
N	5.007695	3.672157	1.944489
C	4.399285	2.840527	3.002644
C	6.426436	3.939431	2.272848
C	4.826037	9.100392	−1.133904
C	6.224885	9.454602	−1.696365
C	4.644126	9.863972	0.192426
C	3.737961	9.588890	−2.119014
C	4.853129	4.555474	−3.323207
C	3.622170	4.962406	−4.173929
C	6.150999	4.908607	−4.091081
C	4.808035	3.025153	−3.177383
H	7.677528	3.226930	−1.296390
H	−9.693667	2.002545	−1.261473
H	7.967298	−1.094905	1.097191

H	5.843522	0.099745	1.025412
H	3.961727	−0.214254	−0.080566
H	1.826636	−1.405702	−0.044602
H	−0.271560	2.342087	0.095045
H	1.862869	3.541136	−0.007818
H	3.206241	4.725207	1.865848
H	4.527178	5.652254	2.581082
H	4.906968	7.183208	−3.040283
H	4.477965	7.562947	1.198856
H	0.049263	−2.003097	1.260743
H	−2.064716	−3.227642	1.295527
H	−3.899172	−0.099917	−1.025230
H	−1.775305	1.094556	−1.097469
H	4.431213	3.351378	3.975961
H	3.362021	2.619690	2.743057
H	4.947154	1.897550	3.075417
H	6.871598	4.570905	1.501955
H	6.498017	4.448970	3.244334
H	6.972494	2.996443	2.306674
H	6.422777	8.951317	−2.647525
H	6.310795	10.535175	−1.862695
H	7.008848	9.159955	−0.990353
H	4.748665	10.939424	0.012808
H	3.654804	9.696811	0.632582
H	5.401919	9.583988	0.931843
H	3.813823	9.098005	−3.093886
H	3.831931	10.668597	−2.281130
H	2.734550	9.389432	−1.727257
H	3.563930	6.041500	−4.343334
H	2.696465	4.650525	−3.677605
H	3.658113	4.468731	−5.152371
H	6.261158	5.983303	−4.263298
H	6.155029	4.411004	−5.067924
H	7.034430	4.566026	−3.540731
H	5.682964	2.629937	−2.653230
H	3.899651	2.680462	−2.672670
H	4.810146	2.564017	−4.171747
Ga	−4.909316	−2.794990	0.089126
C	−6.633059	−1.771347	0.022020
C	−6.699824	−0.366057	0.030545
C	−7.914285	0.319625	0.000888
C	−9.136199	−0.373032	−0.046630
C	−9.085749	−1.777746	−0.049323
C	−7.865575	−2.452263	−0.009183
C	−5.469471	−4.952528	−1.769297
C	−5.037871	−4.712895	0.702902
C	−4.943013	−5.321074	1.975564
C	−4.929284	−6.724717	2.059480
C	−5.022464	−7.573624	0.950220

C	−5.177449	−6.963439	−0.298239
C	−5.196320	−5.571348	−0.407754
N	−4.735165	−3.672204	−1.943969
C	−5.341496	−2.839707	−3.002649
C	−3.316427	−3.941176	−2.270785
C	−4.932057	−9.100572	1.134469
C	−3.534911	−9.459769	1.697978
C	−5.115792	−9.863589	−0.191923
C	−6.022864	−9.584759	2.118747
C	−4.891705	−4.555185	3.322855
C	−6.123331	−4.959471	4.173871
C	−3.594240	−4.910460	4.090381
C	−4.934300	−3.024793	3.176888
H	−5.781155	0.214518	0.079079
H	−7.916369	1.405605	0.043068
H	9.471199	−2.342530	−0.094600
H	−7.879469	−3.541236	0.008512
H	−6.538060	−4.722863	−1.866982
H	−5.217709	−5.651565	−2.581315
H	−4.844521	−7.183294	3.040472
H	−5.274457	−7.562569	−1.198591
H	−5.309108	−3.350419	−3.976013
H	−6.378792	−2.617849	−2.744076
H	−4.792546	−1.897298	−3.074642
H	−2.872630	−4.572801	−1.499213
H	−3.244512	−4.451245	−3.241949
H	−2.769377	−2.998787	−2.304737
H	−3.335813	−8.957293	2.649319
H	−3.452897	−10.540680	1.864216
H	−2.749552	−9.167703	0.992420
H	−5.013734	−10.939348	−0.012639
H	−6.104787	−9.693910	−0.631856
H	−4.357496	−9.585035	−0.931378
H	−5.945115	−9.094944	3.094016
H	−5.934571	−10.665172	2.280041
H	−7.025142	−9.379872	1.726646
H	−6.184311	−6.038406	4.343002
H	−7.048326	−4.645085	3.677885
H	−6.085991	−4.466063	5.152389
H	−3.485528	−5.985382	4.262059
H	−3.589357	−4.413233	5.067407
H	−2.710456	−4.568871	3.539966
H	−4.931816	−2.563676	4.171243
H	−4.058810	−2.630658	2.652873
H	−5.842152	−2.678862	2.672087
Tv [a]	19.485303	0.000000	0.000000

[a] Tv signifies the translation vector of the unit cell employed.

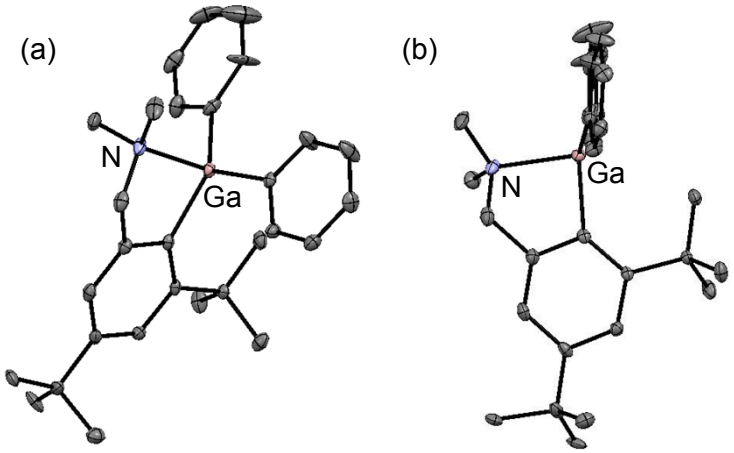


Figure S18. ORTEP drawings of (a) **model 1** and (b) side view (30% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

References

(1) T. Higashi, *ABSCOR. Program for Absorption Correction.*; Rigaku Corporation: Japan, 1995.

(2) G. M. Sheldrick, SHELX-97. Programs for Crystal Structure Analysis.; University of Göttingen: Germany, 1997.

(3) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115.

(4) Wakita, K. *Yadokari-XG. Program for Crystal Structure Analysis.*; 2000.

(5) L. J. Farrugia, *J. Appl. Cryst.* 1997, **30**, 565.

(6) Y. Zhu, R. D. Champion and S. A. Jenekhe, *Macromolecules*, 2006, **39**, 8712.

(7) K. Takagi, K. Saiki, H. Hayashi, H. Ohsawa, S. Matsuoka and M. Suzuki, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 236.

(8) (a) Y M. Yoshifuji, K. Kamijo and K. Toyota, *Tetrahedron Lett.*, 1994, **35**, 3971; (b) B. Bagh, J. B. Gilroy, A. Staubitz and J. Müller, *J. Am. Chem. Soc.*, 2010, **132**, 1794.

(9) A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliteni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115.

(10) G. M. Sheldrick, *SHELX-97 Programs for Crystal Structure Analysis* (University of Göttingen, Göttingen, Germany, 1997).

(11) M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*; Third ed., 2006, 108.

(12) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(13) (a) R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V. R. Saunders and C. M. Zicovich-Wilson, Z. Kristallogr., 2005, 220, 571. (b) R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco and M. Llunell, CRYSTAL09, (2009) CRYSTAL09 User's Manual. University of Torino, Torino.