

Electronic Supporting Information for

**Novel Glassy Tetra(N-alkyl-3-bromocarbazole-6-yl)silanes as Building Blocks
for Efficient and Nonaggregating Blue-Light-Emitting Tetrahedral Materials**

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Part I. Experimental procedures and characterization data on newly synthesized compounds and polymers.

General Information: Unless stated otherwise, all reagents and solvents were of commercial grade, and used as received. All reactions were performed under a purified nitrogen atmosphere using the standard Schlenk technique. Tetrahydrofuran (THF) was distilled over CaH₂ before use. The ¹H NMR spectra were recorded at 25 °C on a Bruker AVANCE 400 spectrometer. Mass spectra were recorded on a Bruker Autoflex TOF/TOF MALDI-TOF MS spectrometer using dithranol/Ag-TFA as a matrix. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using polystyrenes as standards and THF as a mobile phase at 1.0 mL/minute. UV-Vis spectra were measured with a UV-Vis spectrometer (Shimadzu, UV-2501 PC) at 25 °C. Fluorescence spectra were recorded on a LS50B Luminescence Spectrometer (Perkin Elmer) at 25 °C. Glass transition temperatures were determined by differential scanning calorimetry (DSC) experiments using a TA 2920 Modulated DSC instrument with a ramp speed of 10 °C/min. Thermogravimetric analyses (TGA) were conducted on a Perkin Elmer thermogravimetric Analyzer TGA 7 under a heating rate of 20 °C/min and a nitrogen flow rate of 20 cm³/min. WAXS measurements were conducted using Bruker X-ray diffractometer using Cu K α ($\lambda = 1.541 \text{ \AA}$) radiation. Thin films of the samples prepared by a hydraulic press die were used for the measurements. The X-ray tube was operated at 40 kV and 40 mA. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The starting compounds N-alkyl-3,6-dibromocarbazole (alkyl = ethyl, *n*-butyl and *n*-hexyl),¹ 9,9-dihexylfluorene-2-boronic acid and 9,9-dihexylfluorene-2,7-bis(trimethylene boronate)² were prepared according to the literature methods.

Quantum yield determination. The photoluminescent quantum yields (Φ_{PL}) of the compounds in THF were determined using a solution of quinine sulfate as a standard (*ca.* 1×10^{-5} M in 0.1 M H₂SO₄, having a quantum yield of 55%). Dilute sample solutions were used for the determinations (absorbance < 0.1). All samples were degassed before measurements. The correction of emission spectra was carried out by reference to quinine bisulfate in acidic solution (400-600 nm) according to the literature method.³ The Φ_{PL} values of films were determined using 9,10-diphenylanthracene as a standard (dispersed in PMMA films with a concentration lower than 1×10^{-3} M and a quantum efficiency of 83%). Thin films (absorbance < 0.2) were dried at 50 °C under a vacuum oven for 16 h before measurements. Values are calculated according to Equation (1), where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the fluorescence quantum yield of the standard, I_{unk} and I_{std} are the integrated emission intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respectively, and η_{unk} and η_{std} are the refractive indexes of the corresponding solutions (pure solvents were assumed).⁴

$$\Phi_{\text{unk}} = \Phi_{\text{std}}(I_{\text{unk}}/A_{\text{unk}})(A_{\text{std}}/I_{\text{std}})(\eta_{\text{unk}}/\eta_{\text{std}})^2 \dots\dots\dots\text{equation 1}$$

A general procedure for the synthesis of precursors 1-3 by the Grignard method. N-hexyl-3,6-dibromocarbazole (10 g, 24.4 mmol) and Mg (0.62 g, 25.5 mmol) were dissolved in THF (150 mL). The reaction was initiated by addition of I₂. The reaction mixture was stirred at r. t. for

2 h, and then refluxed overnight. The obtained Grignard was cooled to r. t. and was added Si(OMe)₄ (1.03 g, 6.8 mmol) in one portion. The reaction mixture was stirred at r. t. for 2 days, and then refluxed for 4 h. The above reaction solution was cooled to r. t. and was added 30 mL 1N HCl, and then stirred for 0.5 h. The organic layer was isolated, aqueous layer was extracted with dichloromethane (2 × 100 mL). The combined organic layer was washed with 10% NaOH, brine, water, and then dried (MgSO₄). The organic solution was filtered through celite to give a clear yellow solution. The crude product was purified by silica gel column chromatography (chloroform/*n*-hexane 1:1). After separation of the small compounds **1-3**, the polymer residue in column was washed out with ethyl acetate, and was further purified by continuous extraction with acetone using Soxhlet apparatus for 24 h.

A general procedure for the synthesis of precursors 1-3 by mono-lithiation. In a 250 mL 2-necked RBF was added N-hexyl-3,6-dibromocarbazole (6 g, 14.7 mmol) and 100 mL freshly dried THF. The solution was cooled to – 78 °C using dry ice/acetone bath. To the cooled solution was added *n*-BuLi (1.6 M, 11 mL, 17.6 mmol) dropwise through a syringe. The reaction mixture was allowed to stir at – 78 °C for another two hours, and then was added Si(OMe)₄ (0.66 mL, 4.4 mmol) in one portion. The reaction mixture was stirred at – 78 °C for 4 h, and then was allowed to warm to room temperature and stirred for another 5 days. After that, the reaction mixture was refluxed for another 4 h. Upon completion, solvent was removed. The residue was re-dissolved in chloroform (100 mL), and was washed with water and dried (MgSO₄). The chloroform solution was filtered through celite and concentrated to give a yellow solid. The crude product was subjected to column chromatography (chloroform/*n*-hexane 1:1) to give compounds **1-3**. After separation of the small compounds **1-3**, the polymer residue in column was washed out

with ethyl acetate, and was further purified by continuous extraction with acetone using Soxhlet apparatus for 24 h.

Tetra(N-ethyl-3-bromocarbazole-6-yl)silane, 1. A white solid. Anal. Calcd. for $C_{56}H_{44}Br_4N_4Si$: 1120.698. C, 59.90; H, 4.00; Br, 28.52; N, 5.00; found C, 59.92; H, 4.46; Br, 28.16; N, 4.56. 1H NMR ($CDCl_3$): δ 1.45 (t, $^3J_{H-H} = 7.2$ Hz, 12 H), 4.38 (q, $^3J_{H-H} = 7.2$ Hz, 8 H), 7.30 (d, $^3J_{H-H} = 8.4$ Hz, 4 H), 7.47 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 7.53 (dd, $^3J_{H-H} = 8.4$ Hz, $^4J_{H-H} = 1.8$ Hz, 4 H), 7.86 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 8.17 (d, $^4J_{H-H} = 1.8$ Hz, 4 H), 8.43 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.2, 38.1, 108.9, 110.2, 112.2, 122.3, 123.7, 125.0, 125.1, 128.6, 128.8, 133.7, 138.9, 141.8. MALDI-TOF MS (m/z): 1146.4 ($M^+ + Na^+$), 1222.2 ($M^+ + Ag^+$).

Tetra[N-(n-butyl)-3-bromocarbazole-6-yl)silane], 2. A white solid. Anal. Calcd. for $C_{64}H_{60}Br_4N_4Si$: 1232.914. C, 62.35; H, 4.91; Br, 25.92; N, 4.54. Found: C, 62.12; H, 5.14; Br, 25.54; N, 4.36. 1H NMR ($CDCl_3$): δ 0.96 (t, $^3J_{H-H} = 7.2$ Hz, 12 H), 1.42 (m, 8 H), 1.87 (m, 8 H), 4.30 (t, $^3J_{H-H} = 7.2$ Hz, 8 H), 7.29 (d, $^3J_{H-H} = 8.8$ Hz, 4 H), 7.46 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 7.52 (dd, $^3J_{H-H} = 8.8$ Hz, $^4J_{H-H} = 1.8$ Hz, 4 H), 7.84 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 8.15 (d, $^4J_{H-H} = 1.8$ Hz, 4 H), 8.41 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.2, 20.9, 31.5, 43.4, 109.1, 110.5, 112.2, 122.2, 123.6, 125.0, 128.6, 128.7, 133.7, 139.5, 142.3. MALDI-TOF MS (m/z): 1230.6 (M^+), 1258.5 ($M^+ + Na^+$), 1338.5 ($M^+ + Ag^+$).

Tetra[N-(n-hexyl)-3-bromocarbazole-6-yl)silane], 3. A white solid. Anal. Calcd. for $C_{72}H_{76}Br_4N_4Si$: 1345.13. C, 64.29; H, 5.70; Br, 23.76; N, 4.17. Found: C, 64.00; H, 5.33; Br, 23.69; N, 4.21. 1H NMR ($CDCl_3$): δ 0.87 (t, $^3J_{H-H} = 6.8$ Hz, 12 H), 1.31 (m, 16 H), 1.34 (m, 8 H), 1.87 (m, 8 H), 4.30 (t, $^3J_{H-H} = 6.8$ Hz, 8 H), 7.29 (d, $^3J_{H-H} = 8.8$ Hz, 4 H), 7.47 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 7.53 (dd, $^3J_{H-H} = 8.8$ Hz, $^4J_{H-H} = 2.0$ Hz, 4 H), 7.84 (d, $^3J_{H-H} = 8.0$ Hz, 4 H), 8.16 (d, $^4J_{H-H} =$

2.0 Hz, 4 H), 8.41 (s, 4 H). ^{13}C NMR (CDCl_3): δ 14.4, 22.9, 27.3, 29.3, 31.9, 43.6, 109.2, 110.5, 112.2, 122.2, 123.6, 124.4, 125.0, 128.6, 128.7, 133.6, 139.5, 142.3. MALDI-TOF MS (m/z): 1352.6 ($\text{M}^+ + 7$), 1374.4 ($\text{M}^+ + \text{Na}^+$), 1488.6 ($\text{M}^+ + \text{Ag}^+$).

P1. A gray powder. ^1H NMR (CDCl_3): δ 1.46 (br.), 4.38 (br.), 6.8-8.8 (m). ^{13}C NMR (CDCl_3): δ 14.1, 38.0, 108.6, 108.8, 110.2, 112.2, 119.3, 120.9, 122.2, 123.3, 123.7, 125.1, 125.9, 128.3, 128.6, 128.8, 133.1, 133.8, 138.9, 141.7.

P2. A gray powder. ^1H NMR (CDCl_3): δ 0.94 (br.), 1.30 (br.), 1.82 (br.), 4.23 (br.), 7.0-8.8 (m). ^{13}C NMR (CDCl_3): δ 14.2, 20.8, 31.4, 43.2, 108.8, 109.0, 110.4, 112.1, 119.0, 120.7, 120.9, 122.1, 123.2, 123.6, 124.9, 125.9, 126.7, 128.1, 128.4, 128.6, 132.7, 133.3, 139.4, 142.1.

P3. A gray powder. ^1H NMR (CDCl_3): δ 0.83 (br.), 1.24 (br.), 1.69 (br.), 4.06 (br.), 6.9-8.7 (m). ^{13}C NMR (CDCl_3): δ 14.3, 22.8, 27.2, 29.2, 31.8, 43.3, 108.7 (br.), 110.3 (br.), 111.7 (br.), 119.1 (br.), 120.6 (br.), 121.7 (br.), 123.2 (br.), 124.8 (br.), 126.5 (br.), 128.0 (br.), 132.8 (br.), 139.1 (br.), 141.9 (br.).

Synthesis of tetra{[(9,9-dihexyl-3-fluorenyl)-N-hexyl]carbazole-6-yl}silane, 4. Compound **3** (0.4 g, 0.30 mmol), 9,9-dihexylfluorene-2-boronic acid (0.55 g, 1.45 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (20 mg, 1 mol%) were dissolved in toluene (6 mL) and 2 M aq. K_2CO_3 (4 mL). The reaction mixture was degassed by bubbling with N_2 for 15 minutes, and then was heated at 90-100 $^\circ\text{C}$ for 2 days. Upon completion, the organic layer was separated, and was washed with water and dried (MgSO_4). The product was isolated by silica gel column chromatography (chloroform/*n*-hexane 1:2, $R_f = 0.25$) and was obtained as a white solid in 60% yield (0.42 g). Anal. Calcd. for $\text{C}_{172}\text{H}_{208}\text{N}_4\text{Si}$: 2359.67. C, 87.55; H, 8.89; N, 2.37. Found: C, 87.10; H, 8.97; N, 2.37. ^1H NMR (CDCl_3): δ 0.72 (t, $^3J_{\text{H-H}} = 7.0$ Hz, 24 H), 0.87 (t, $^3J_{\text{H-H}} = 6.8$ Hz, 12 H), 1.03 (m, 64 H), 1.33 (m, 16 H), 1.45 (m, 8 H), 1.93 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 8 H), 2.00 (m, 16 H), 4.36 (t, $^3J_{\text{H-H}} = 7.2$ Hz, 8 H), 7.29 (d, $^3J_{\text{H-H}} = 7.6$

Hz, 4 H), 7.32 (dd, $^3J_{\text{H-H}} = ^3J_{\text{H-H}'} = 7.6$ Hz, 8 H), 7.50 (d, $^3J_{\text{H-H}} = 8.8$ Hz, 8 H), 7.64-7.74 (m, 16 H), 7.79 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 4 H), 7.88 (d, $^3J_{\text{H-H}} = 8.4$ Hz, 4 H), 8.40 (s, 4 H), 8.68 (s, 4 H). ^{13}C NMR (CDCl_3): δ 14.3, 22.9, 24.1, 27.4, 29.4, 30.0, 31.8, 31.9, 40.8, 43.7, 55.5, 109.0, 109.2, 119.4, 119.9, 120.2, 121.9, 123.2, 123.5, 123.9, 124.3, 125.7, 126.4, 127.0, 128.6, 133.5, 139.9, 140.3, 141.3, 141.4, 142.6, 151.3, 151.7. MALDI-TOF MS (m/z): 2355.0 ($\text{M}^+ - 4$).

Synthesis of polymer 5. Compound **3** (0.4 g, 0.3 mmol), 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (0.3 g, 0.6 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (14 mg, 1 mol%) were dissolved in toluene (20 mL) and 2 M aq. K_2CO_3 (14 mL). The reaction mixture was degassed by bubbling with N_2 for 15 minutes, and then was heated at 90-100 °C for 2 days. Upon completion, the organic layer was separated, and was washed with water and dried (MgSO_4). After removal of the organic solvent, the solid was continuously extracted with acetone for 48 h using Soxhlet apparatus (the catalyst residue, unreacted monomers and low molecular oligomers were dissolved in acetone). The remaining solid residue was then extracted with THF for 24 h. The THF solution was concentrated to give the soluble polymer **5** in 38% yield (0.2 g) as a yellow solid. Anal. Calcd. for $(\text{C}_{122}\text{H}_{140}\text{N}_4\text{Si}\bullet 4\text{H}_2\text{O})_n$: (1762.636) $_n$. C, 83.13; H, 8.46; N, 3.18. Found: C, 83.22; H, 8.66; N, 3.38; Br, 1.92 (from residual end groups). ^1H NMR (CDCl_3): δ 0.72 (br., 12 H), 0.87 (br., 12 H), 1.03 (br., 32 H), 1.32 (br., 24 H), 1.93 (br., 8 H), 2.05 (br., 8 H), 4.36 (br., 8 H), 7.50 (br., 12 H), 7.65 (br., 20 H), 7.79 (br., 4 H), 7.86 (br., 4 H), 8.41 (br., 4 H), 8.70 (br., 4 H). ^{13}C NMR (CDCl_3): δ 14.4, 21.5, 22.9, 24.1, 27.3, 29.4, 30.0, 30.7, 31.8, 31.9, 34.6, 40.8, 43.6, 55.6, 109.0, 109.2, 119.4, 120.1, 121.9, 123.2, 123.5, 123.8, 124.3, 125.9, 126.4, 127.0, 127.2, 128.6, 129.2, 133.4, 136.2, 139.8, 140.3, 141.0, 142.6, 152.0.

References:

- (1) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2004**, *16*, 2165.
- (2) Liu, B.; Yu, W.-L.; Lai, Y.-H.; Huang, W. *Macromolecules* **2000**, *33*, 8945.
- (3) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.
- (4) Joshi, H. S.; Jamshidi, R.; Tor, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 2721.

Part II. Table and spectroscopic information for newly synthesized compounds and polymers.

Table S1. Synthesis, thermal and optical properties of precursors **1-3**^a

	yield (%)		M _w (M _w /M _n)	T _g ^c (°C)	T _d ^d (°C)	abs.		em. ^e
	conditions i ^b	conditions ii ^b				λ _{max} (nm)	log ε _{max}	λ _{max} (nm) (fwhm/nm)
1	8	43	-----	137	250	277, 304, 340, 356	5.15, 4.78, 4.17, 4.15	378, 394 (49)
P1	42	12	3820 (1.1)	135	379	276, 301, 334	-----	414 (78)
2	9	41	-----	96	368	277, 304, 340, 356	5.14, 4.75, 4.18, 4.16	377, 394 (46)
P2	40	10	5520 (1.5)	119	358	278, 302, 335	-----	417 (69)
3	9	41	-----	65	434	278, 304, 340, 356	5.18, 4.78, 4.20, 4.20	379 (47)
P3	38	11	7880 (1.8)	109	403	278, 303, 339	-----	395 (67)

^a Sample concentrations for **1-3** were $1.75\text{-}2.23 \times 10^{-5}$ M and for **P1-P3** were 1.0×10^{-2} g/L. ^b

Conditions i and ii refer to those described in Scheme 1. ^c The middle temperatures; ^d T_d is defined as the temperature at which a 5% weight loss is recorded by the TGA analysis. ^e The excitation wavelengths were 301 – 304 nm.

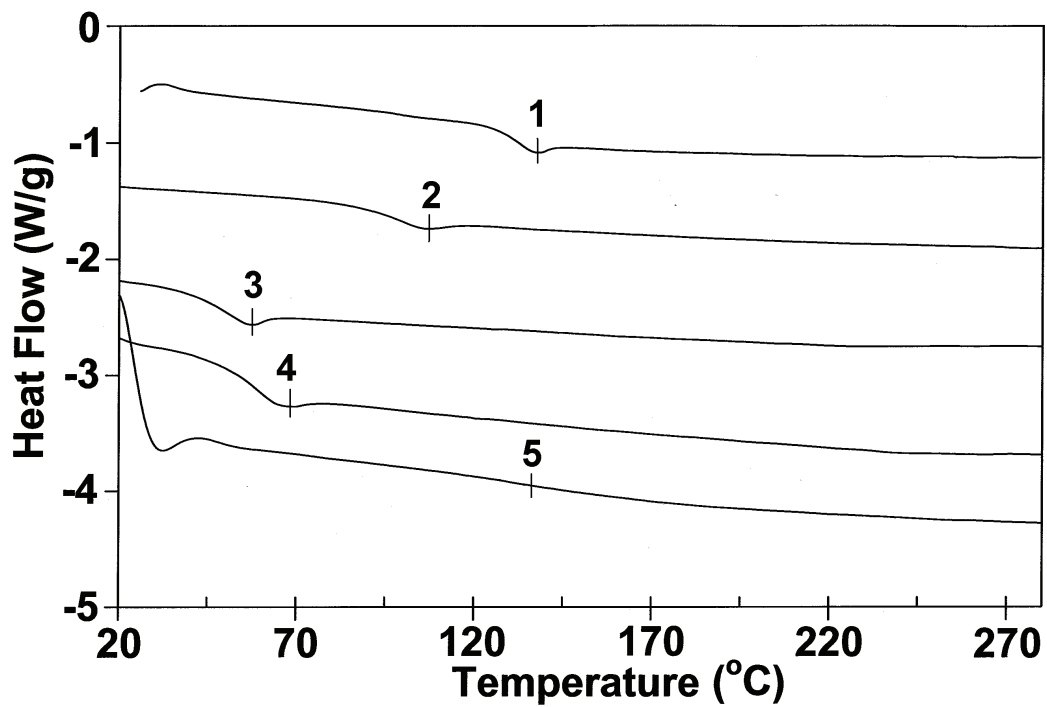


Figure S1. DSC thermograms of **1-5** measured under nitrogen at a heating rate of 10 °C/min (recorded during the second heating scan).

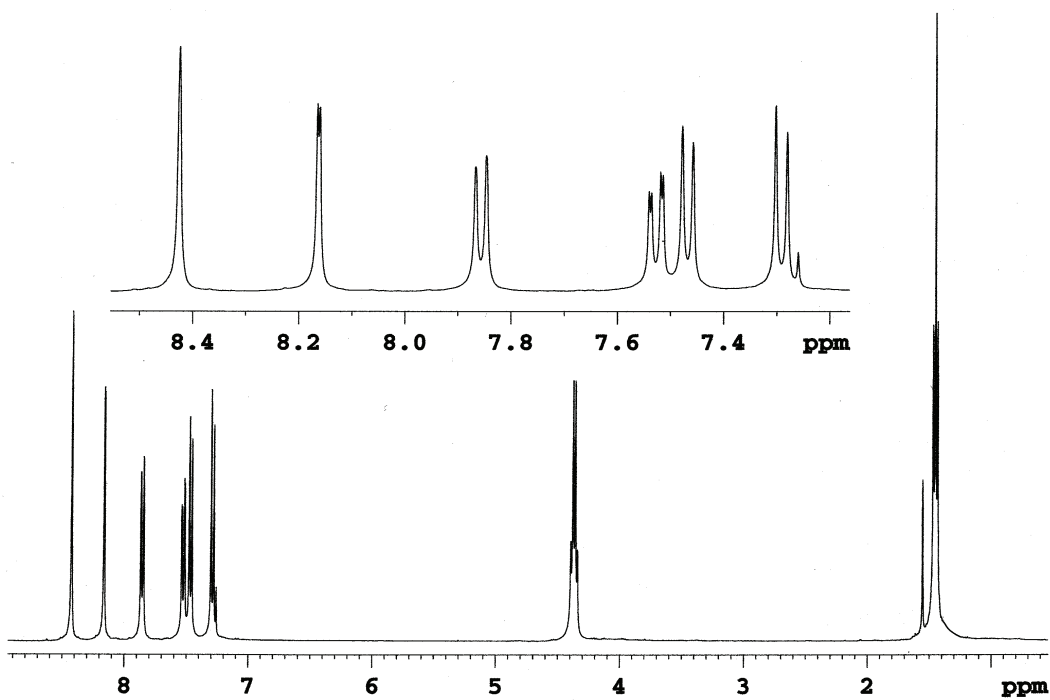


Figure S2. ¹H NMR spectrum of tetrahedral precursor **1** in CDCl₃.

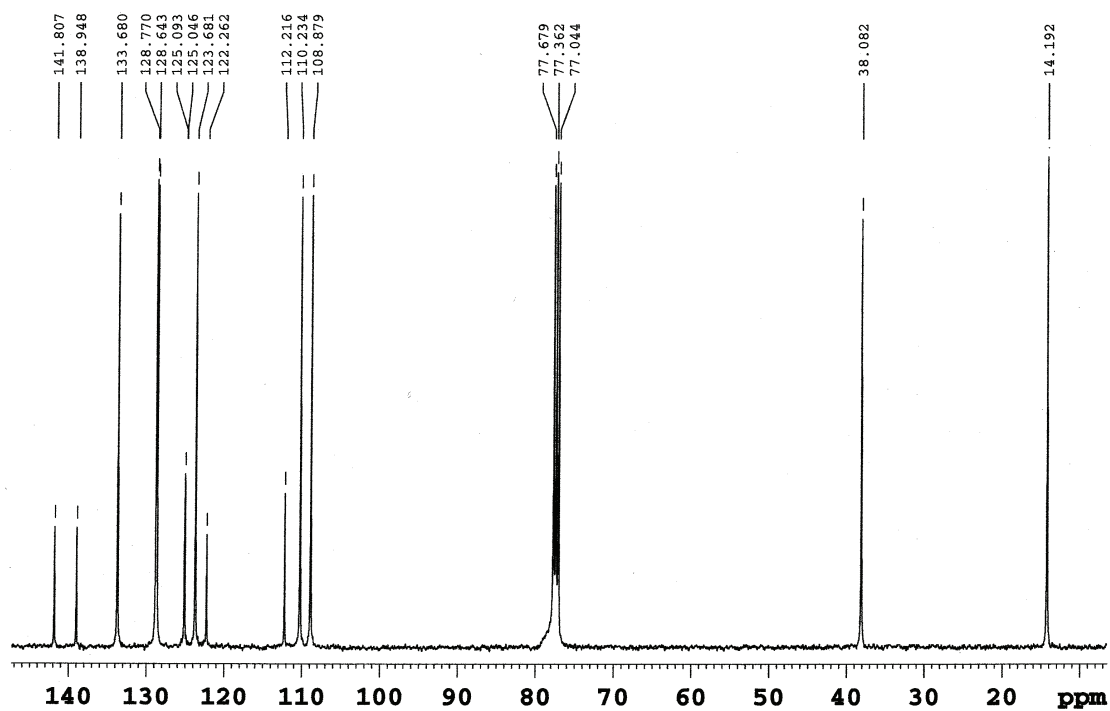


Figure S3. ^{13}C NMR spectrum of tetrahedral precursor **1** in CDCl_3 .

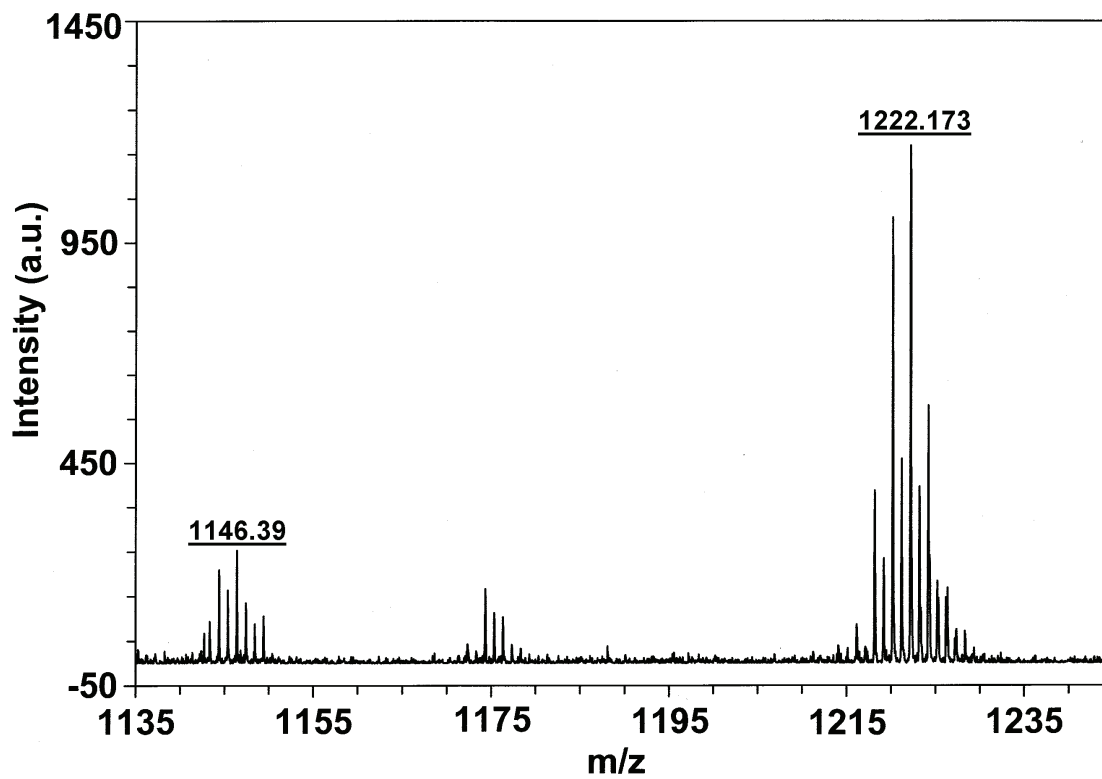


Figure S4. MALDI-TOF MS spectrum of tetrahedral precursor **1**.

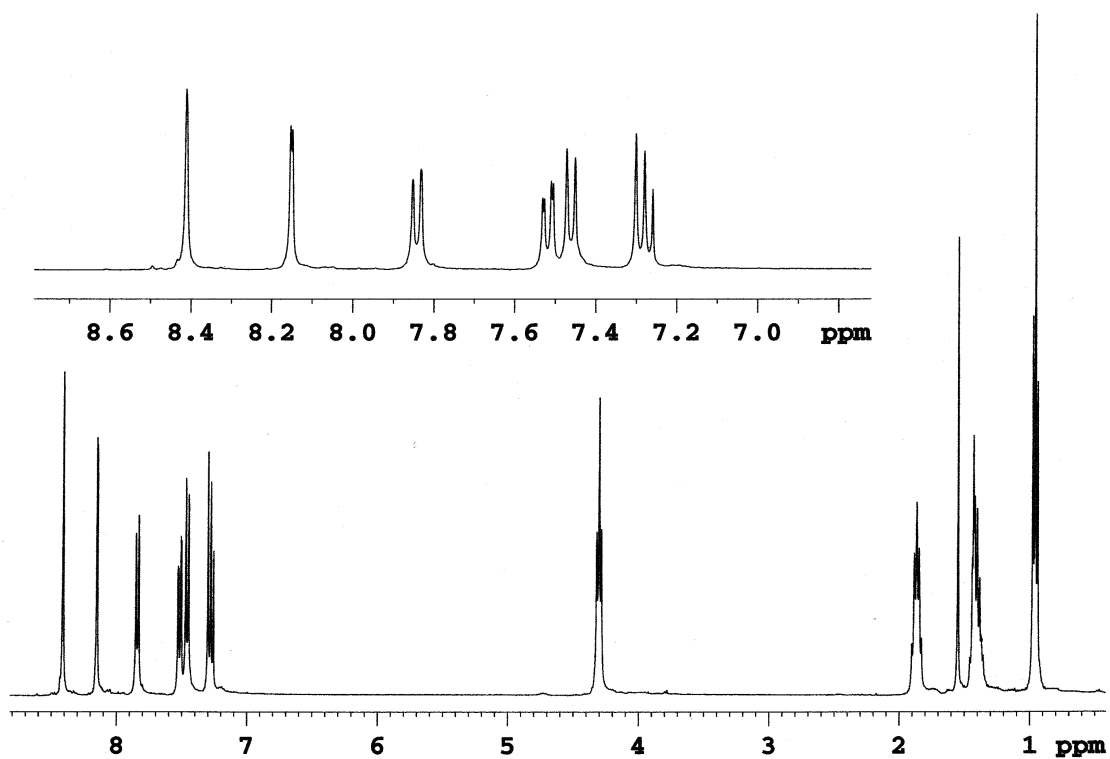


Figure S5. ^1H NMR spectrum of tetrahedral precursor 2 in CDCl_3 .

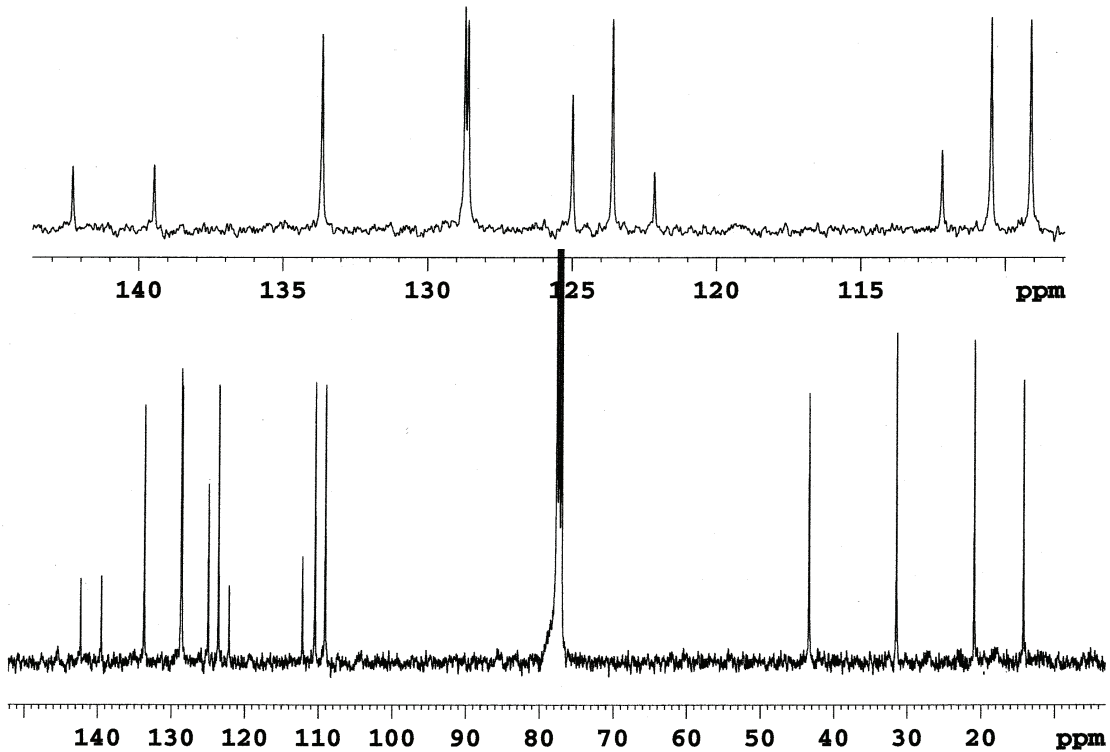


Figure S6. ^{13}C NMR spectrum of tetrahedral precursor 2 in CDCl_3 .

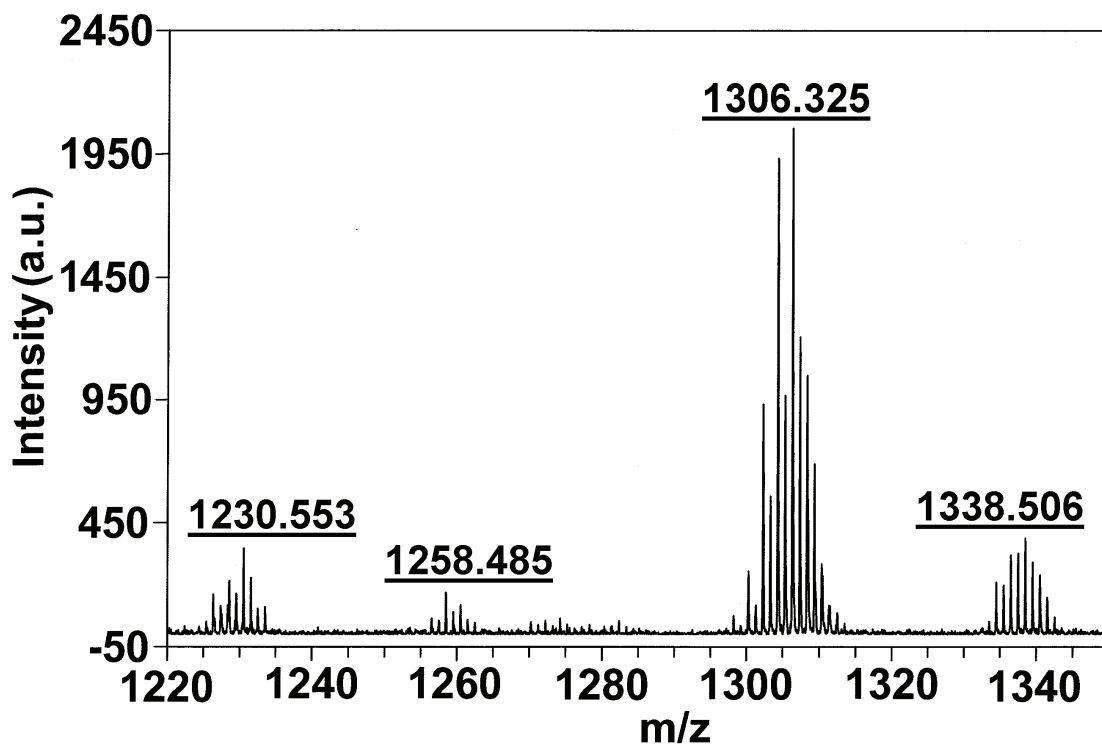


Figure S7. MALDI-TOF MS spectrum of tetrahedral precursor 2.

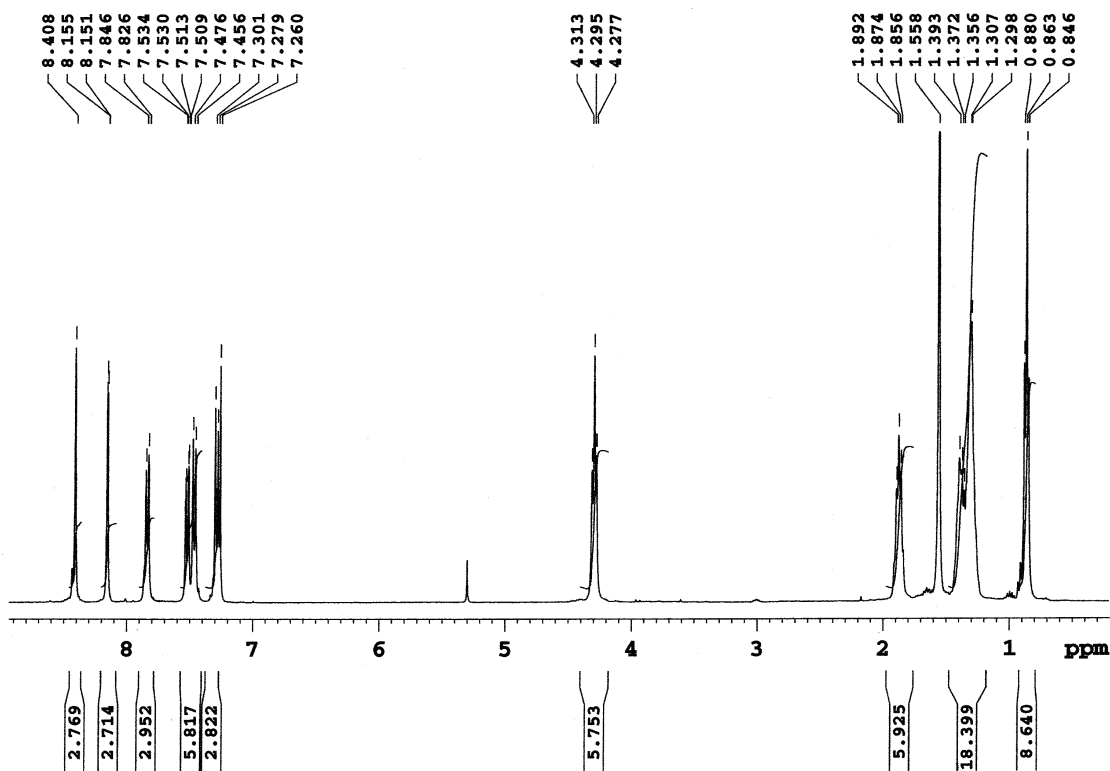


Figure S8. ^1H NMR spectrum of tetrahedral precursor 3 in CDCl_3 .

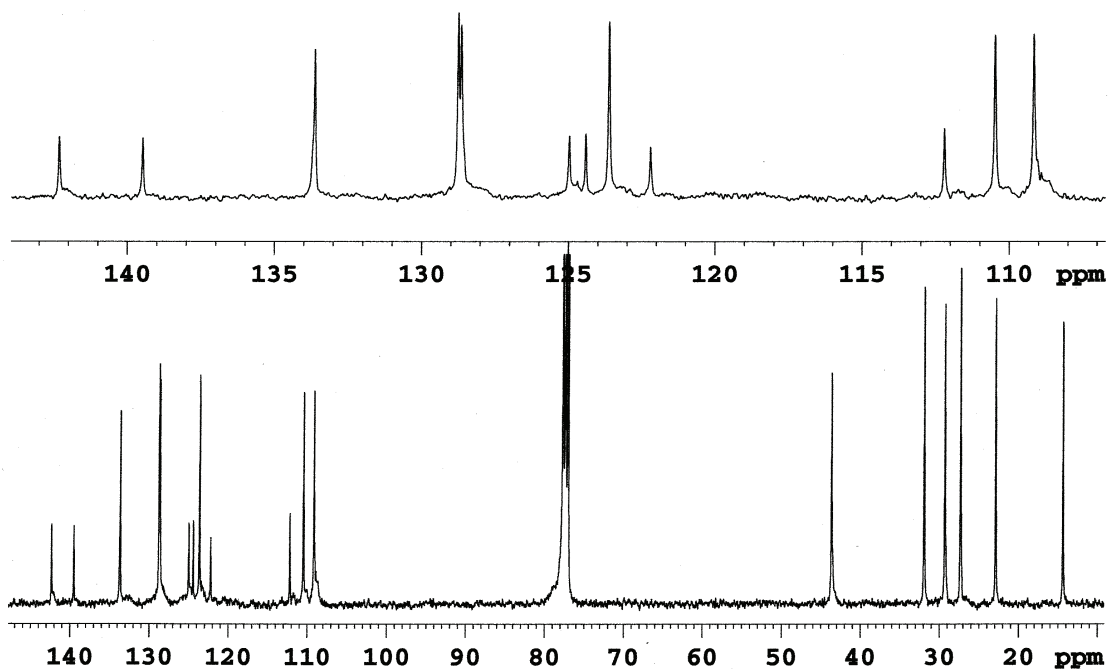


Figure S9. ^{13}C NMR spectrum of tetrahedral precursor 3 in CDCl_3 .

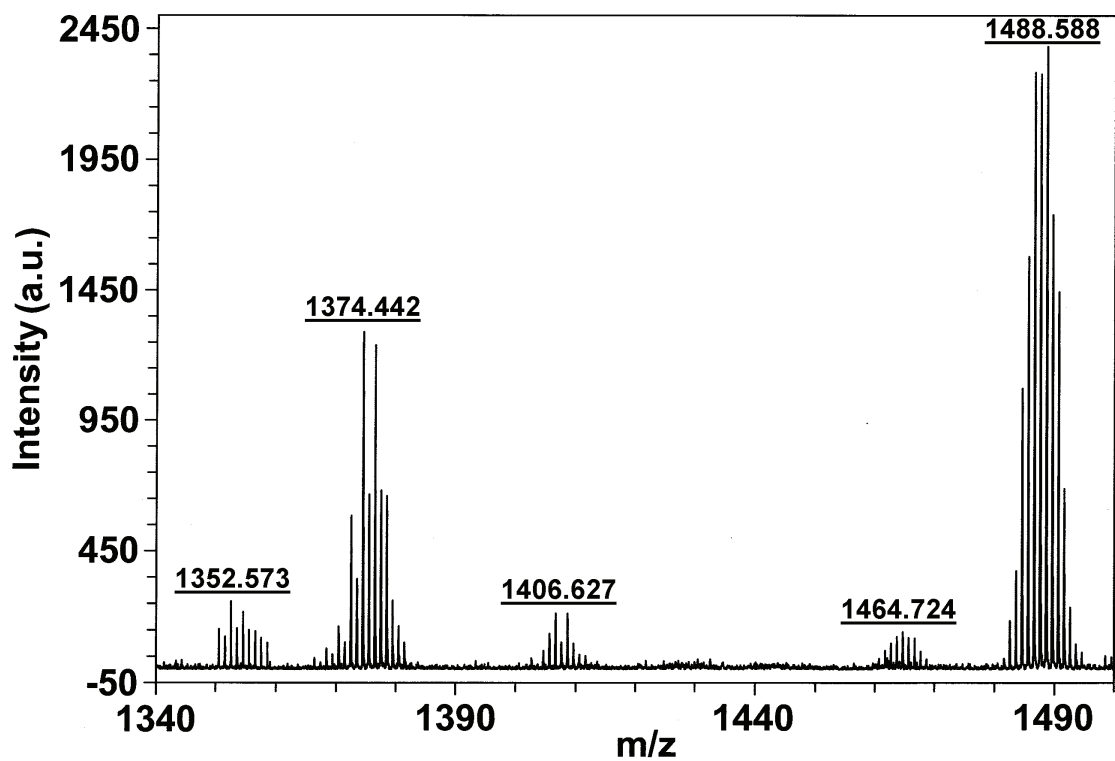


Figure S10. MALDI-TOF MS spectrum of tetrahedral precursor 3.

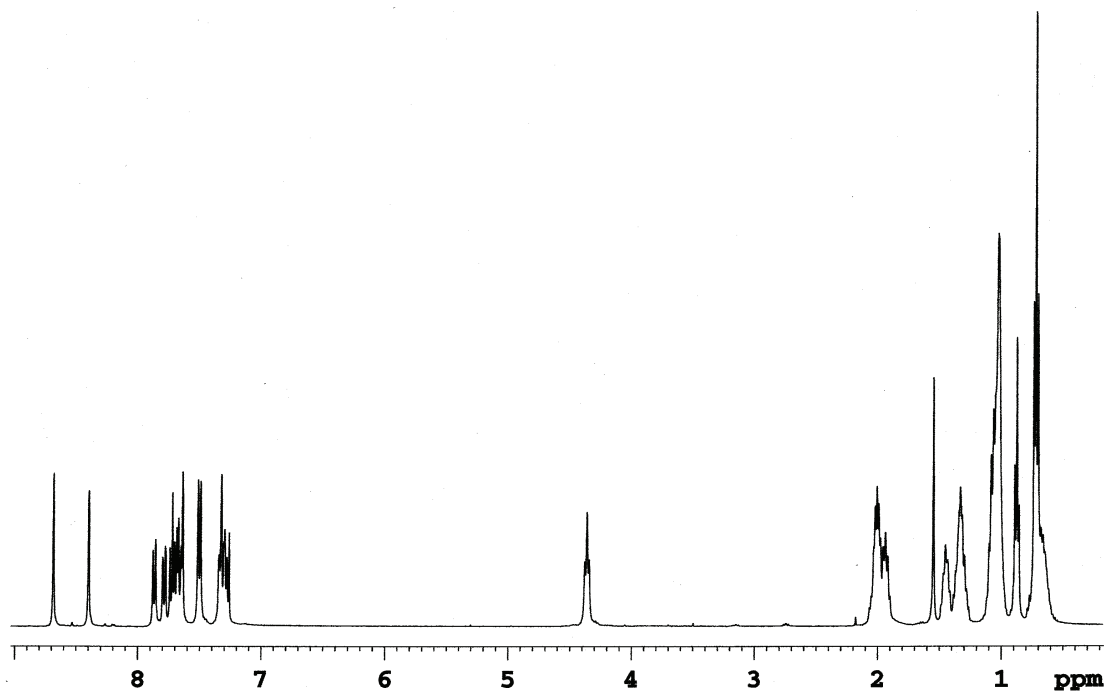


Figure S11. ^1H NMR spectrum of blue-light-emitting molecule 4 in CDCl_3 .

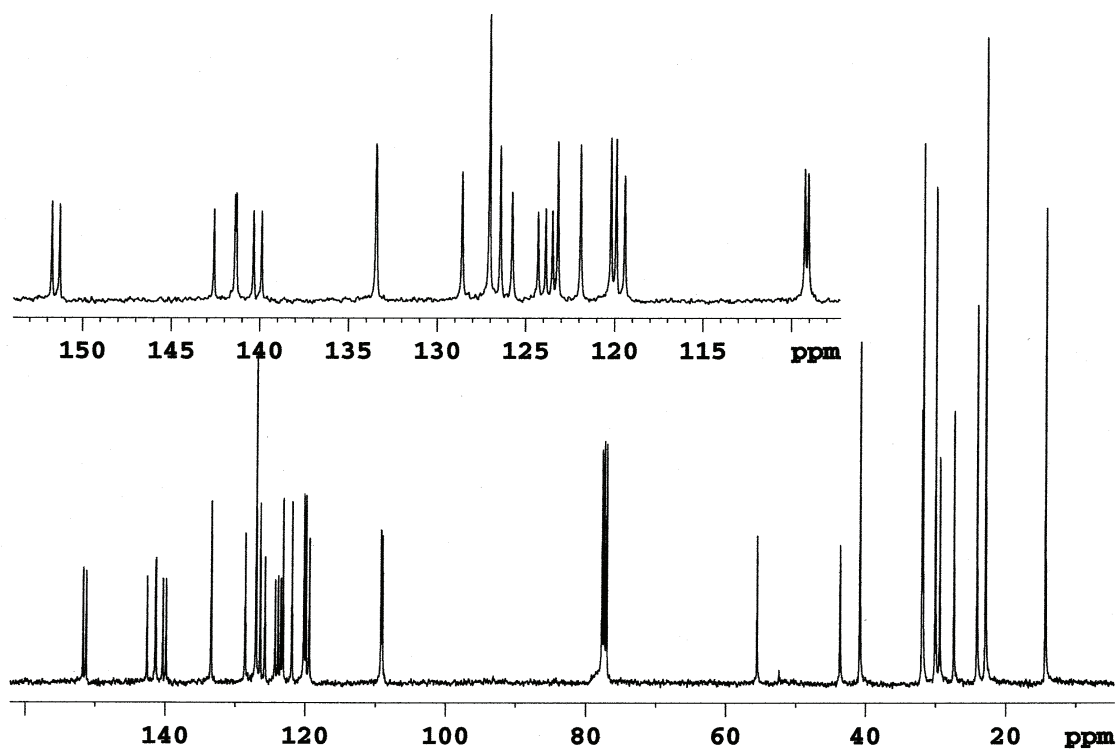


Figure S12. ^{13}C NMR spectrum of blue-light-emitting molecule 4 in CDCl_3 .

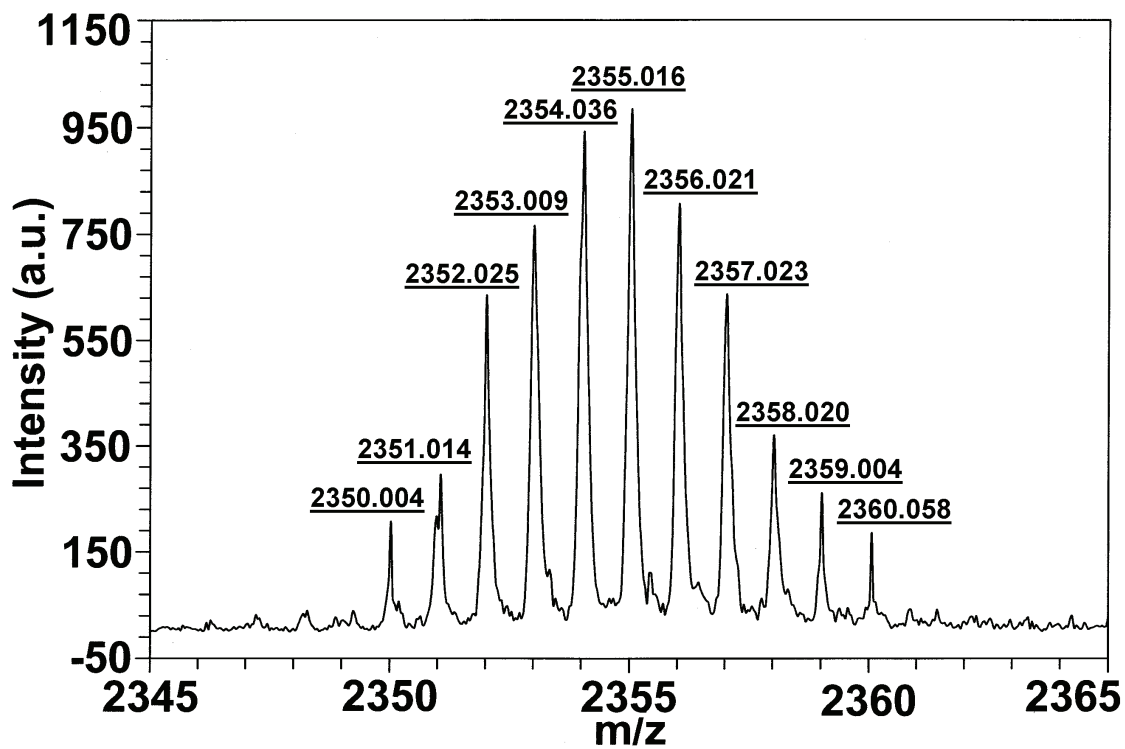


Figure S13. MALDI-TOF MS spectrum of blue-light-emitting molecule 4.

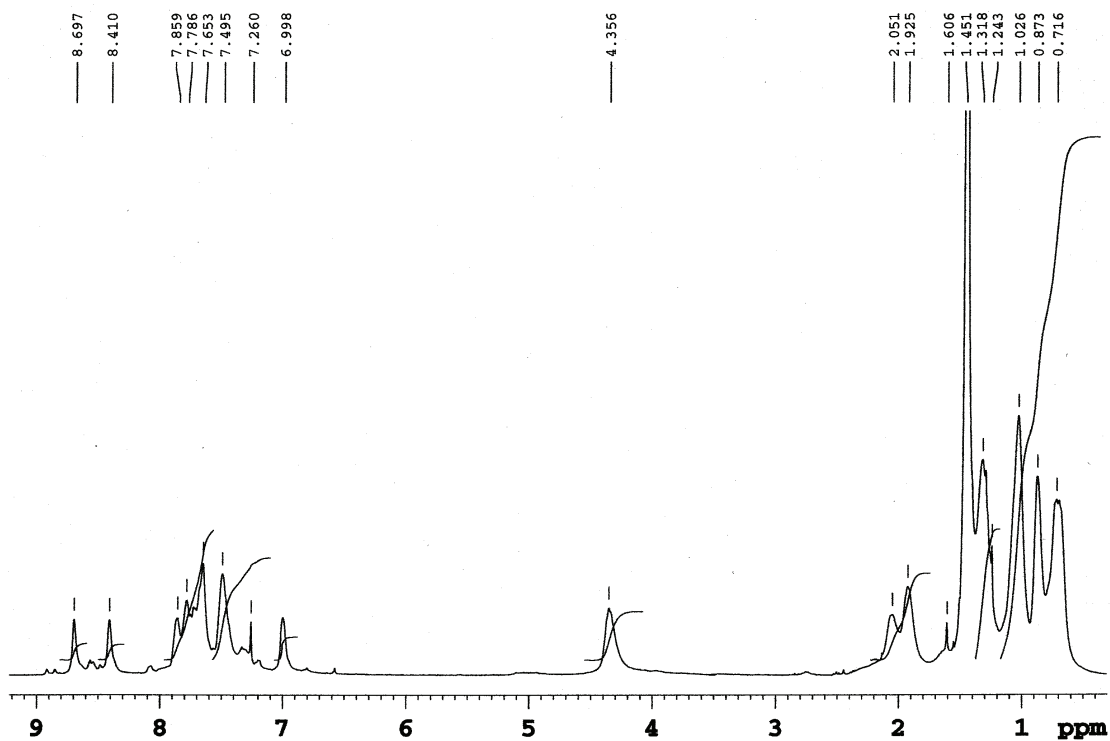


Figure S14. ^1H NMR spectrum of blue-light-emitting polymer 5 in CDCl_3 .

CBZ-C3-hexyl-fluorene-hyperbranched polymer CDC13

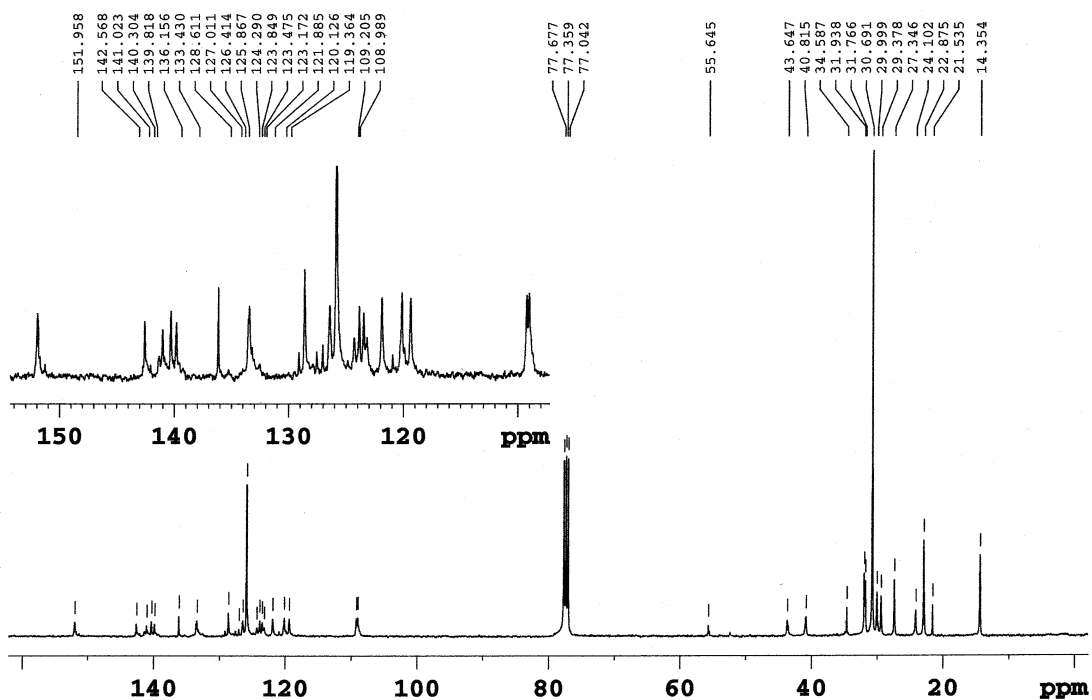


Figure S15. ^{13}C NMR spectrum of blue-light-emitting polymer 5 in CDCl_3 .

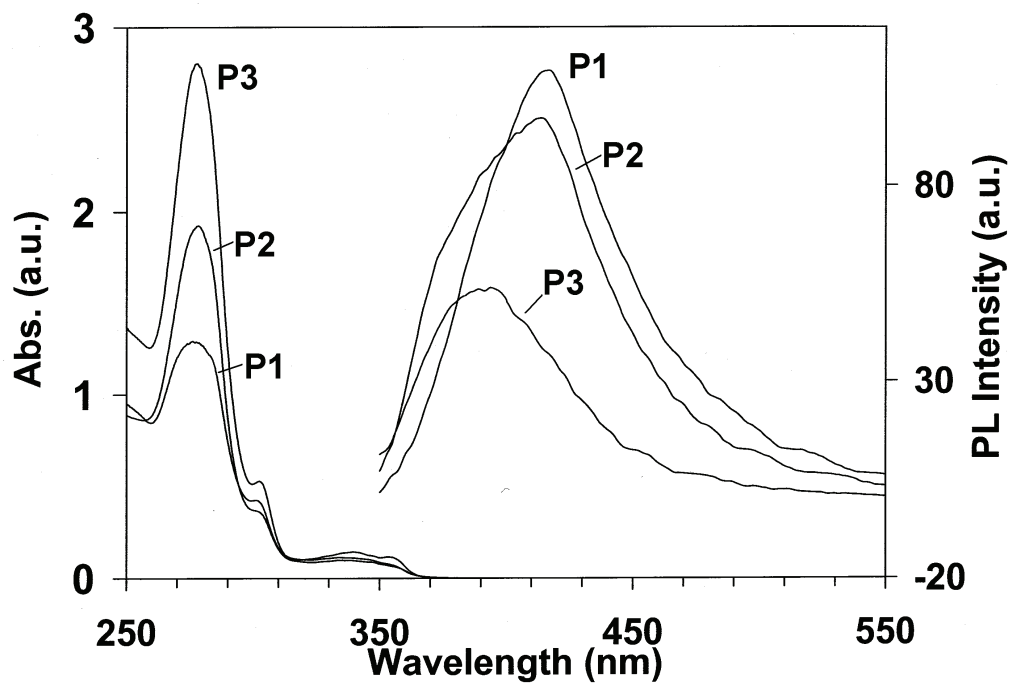


Figure S16. UV and PL emission spectra of P1-P3 in THF.

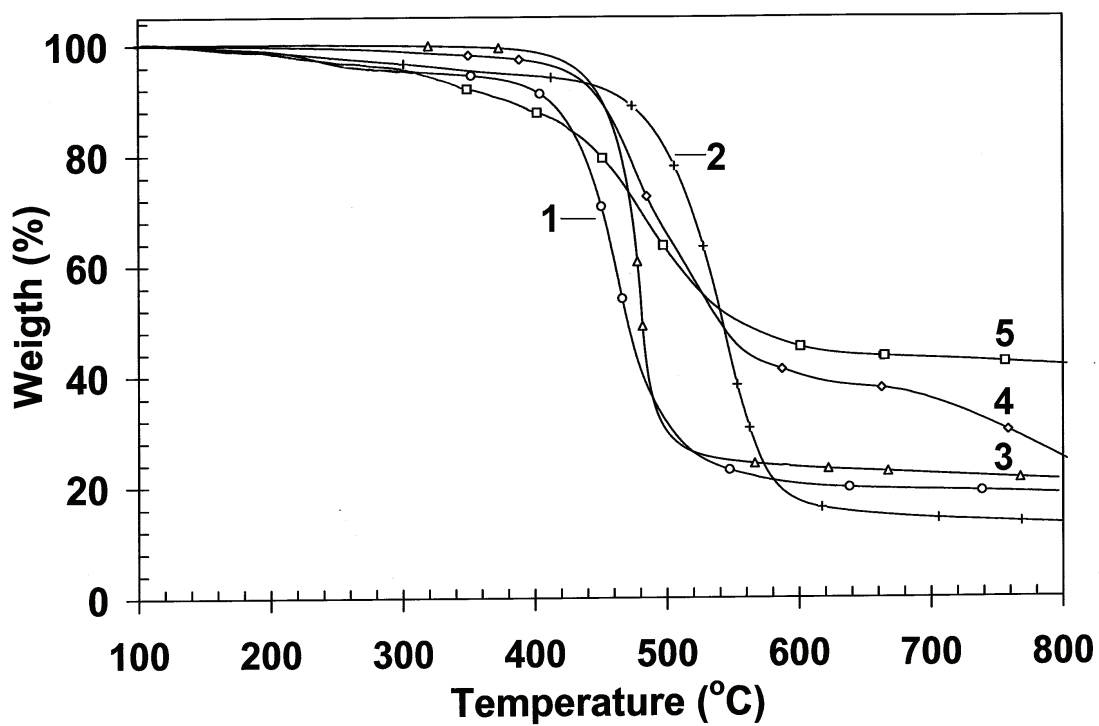


Figure S17. TGA thermograms of 1-5. The thermal analyses were carried out under nitrogen at a heating rate of 20 °C/min.