

Non-Coplanar 9,9-Diphenyl-Substituted Oligofluorenes with Large Two-Photon Absorption Enhancement

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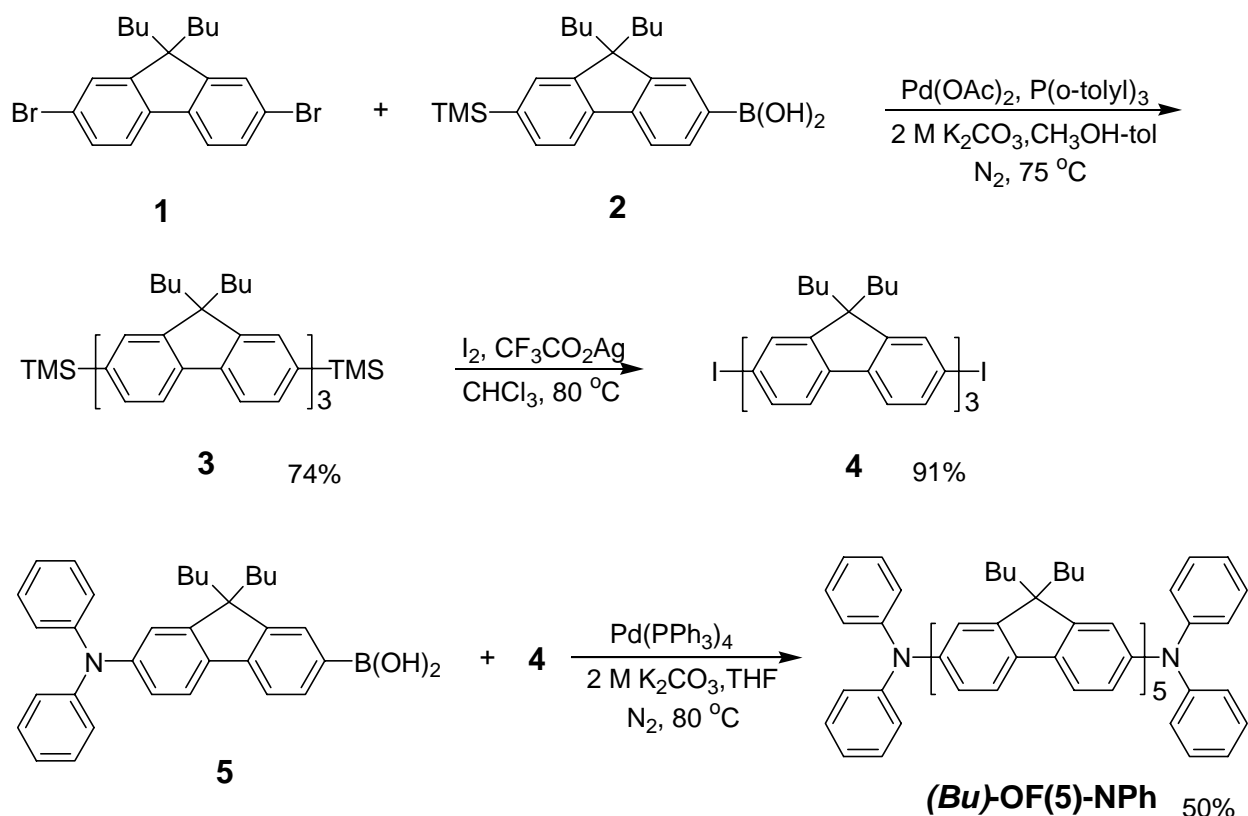
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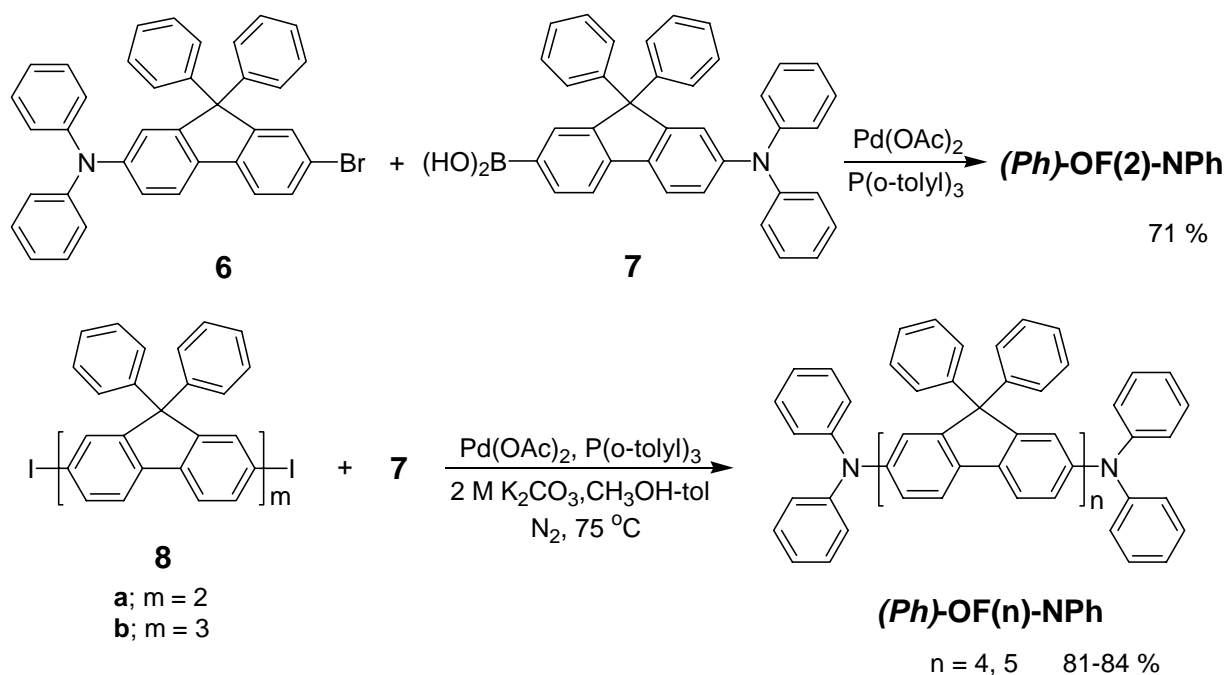
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1. Synthesis

Syntheses of **(Bu)-OF(n)-NPh**, $n = 2-4$ ¹ and **(Ph)-OF(3)-NPh**² reported previously were followed. The synthetic routes for **(Bu)-OF(5)-NPh** and **(Ph)-OF(n)-NPh** $n = 2, 4-5$ are outlined in Scheme 1 and Scheme 2, respectively. Double palladium-catalyzed Suzuki cross-coupling of 2,7-dibromofluorene **1** with 2-(trimethylsilyl)-7-fluorenylboronic acid **2** using Pd(OAc)₂/2P(*o*-tolyl)₃ as a catalyst afforded TMS-substituted terfluorene **3** in 74% yield. Iododesilylation of **3** was carried out in the presence of silver trifluoroacetate at 80 °C affording the corresponding iodide **4** in an excellent yield. Double palladium-catalyzed Suzuki cross-coupling of 7-diphenylamino-9,9-di-*n*-butyl-fluorenyl-2-boronic acid **5** and diiodoterfluorene **4** using Pd(PPh₃)₄ as a catalyst gave **(Bu)-OF(5)-NPh** in a moderate yield (50 %).



Scheme 1. Synthesis of **(Bu)-OF(5)-NPh**



Scheme 2. Synthesis of **(Ph)-OF(n)-NPh**, $n = 2, 4,$ and 5

By adapting a similar convergent approach², 9,9-diphenyl-substituted oligofluorenes were synthesized accordingly. Palladium-catalyzed Suzuki cross-coupling of 7-diphenylamino-9,9-diphenylfluorenyl-2-boronic acid **7** and its precursor bromide **6** afforded **(Ph)-OF(2)-NPh** in 71% yield. In addition, **(Ph)-OF(4)-NPh** and **(Ph)-OF(5)-NPh** were synthesized by double palladium-catalyzed Suzuki cross-coupling of boronic acid **7** and the corresponding diiodobifluorene **8a** and diiodoterfluorene **8b** which afforded the desirable oligofluorenes in 81% and 84% yields, respectively

2. Experimental procedures

General: Fluorescence quantum yields were measured by the relative method using either quinine sulfate in 1.0 M aqueous H_2SO_4 ($\phi_{334} = 0.56$) or 9,10-diphenylanthracene in cyclohexane ($\phi_{360} = 0.90$) or fluorescein in 0.1 M NaOH ($\phi_{436} = 0.92$) as a reference. In these measurements, the slit widths were adjusted so that the spectral bandwidth of the absorption and emission instruments were identical at 1.0 nm, and the absorbance of the sample and the

reference were chosen so they were in the 0.1-0.2 range and nearly identical at the same excitation wavelength. Emission quantum yields were then calculated according to the method described by Crosby and Demas, taking into account the differences between the refractive indices of the sample and reference solutions. Thermal stabilities were determined by thermal gravimetric analyzer with heating rate of 10 °C/min under N₂. For the femto-second-pulse experiment, a self mode-locked Ti-sapphire laser (pulsed width 80-100fs, repetition rate 82 MHz in quasi-continuous-wave) was used as the excitation source to measure the two-photon cross sections. The scanning range can be tuned from 750 to 850 nm. The fundamental wavelength 800 nm was modulated by a chopper for focused on the material in a quartz cell. These respond signals are collected by PMT and transferred to Lock-in-Amplifier for recording the results by computer. In addition, regenerative amplifier can amplify the energy up to ten thousand times of peak energy (1mJ) to perform further experiments. Rhodamine 6G in methanol ($\sigma_{800} = 134 \text{ GM}$) was used as the reference standard. The concentrations of the all solutions were diluted in the range 10^{-4} to 10^{-6} M. The experimental uncertainty of the absolute TPA cross-sections has been determined to be $\pm 15\%$ which was estimated from several independent measurements.

3. A mixture of 2,7-dibromo-9,9-bis(*n*-butyl)fluorene, **2** (1.12 g, 2.57 mmol), 9,9-di(*n*-butyl)-7-(trimethylsilyl)-2-fluorenylboronic acid **1** (3.0 g, 7.72 mmol), palladium (II) acetate (29 mg, 0.13 mmol), tri-(*o*-tolyl)phosphine (79 mg, 0.26 mmol), 2 M K₂CO₃ (15 mL) in toluene (30 mL) and methanol (15 mL) was stirred under a nitrogen atmosphere at 80°C for overnight. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na₂SO₄. Evaporation of volatiles gave a brown solid which was purified by silica gel column chromatography using petroleum ether/dichloromethane as gradient eluent affording **3** in 74 % yield (1.95 g) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 7.2 Hz, 2 H), 7.62-7.67 (m, 8 H), 7.48-7.51(m, 4 H), 2.00-2.11 (m, 12

H), 1.07-1.16 (m, 12 H), 0.67-0.83 (m, 30 H), 0.31(s, 18 H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.8, 151.7, 150.2, 141.5, 140.6, 140.5, 140.4, 140.0, 139.0, 131.9, 128.7, 127.6, 126.1, 126.0, 121.4, 120.1, 120.0, 119.0, 55.3, 55.0, 40.3, 40.0, 26.9, 26.1, 23.1, 23.0, 13.83, 13.78, -0.83. MS (FAB) m/z 975.5 (M^+).

4. A mixture of **3** (1.31 g, 1.34 mmol), silver trifluoroacetate (0.71 g, 3.22 mmol) in chloroform (20 mL) was refluxed for 0.5 h. Iodine was then added in one portion in the solution mixture. The solution mixture was refluxed for another 2 h. After cooling to room temperature, the reaction mixture was poured into a large amount of water and extracted with dichloromethane (3×50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether as eluent. The diiodide **4** was obtained as a white solid with an isolated yield of 91 % (1.32 g). ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.0$ Hz, 2 H), 7.75 (d, $J = 8.0$ Hz, 2 H), 7.60-7.68 (m, 12 H), 7.48 (d, $J = 8.4$ Hz, 2 H), 1.93-2.11 (m, 12 H), 1.08-1.17 (m, 12 H), 0.63-0.73 (m, 30 H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.4, 151.8, 150.9, 141.0, 140.4, 140.2, 140.1, 139.3, 135.9, 132.0, 126.2, 126.1, 121.5, 121.4, 121.3, 120.1, 120.0, 92.5, 55.3, 55.2, 40.2, 40.1, 26.1, 25.9, 23.1, 23.0, 13.8. MS (FAB) m/z 1082.8 (M^+).

(Bu)-OF(5)-NPh. To a solution of **4** (0.38 g, 0.35 mmol), 9,9-bis(*n*-butyl)-2-diphenylamino-7-fluorenylboronic acid **5** (0.52 g, 1.06 mmol), and 2 M K_2CO_3 (2 mL) in THF (25 mL) was added tetrakis(triphenylphosphine)palladium(0) (40mg, 0.035 mmol) under N_2 . After heating at 80°C overnight, the reaction mixture was poured into cool water and extracted with chloroform (3×50 mL). The combined organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether/ CH_2Cl_2 as gradient eluent affording the desired product as a pale yellow solid in 50 % (0.30 g) yield. ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.85 (m, 6 H), 7.65-7.72 (m, 16 H), 7.61 (d, $J = 8.4$ Hz, 4 H), 7.23-7.28 (m, 8 H), 7.15 (d, $J = 7.6$ Hz, 10 H), 7.00-7.07 (m, 6 H), 2.13-2.15 (m, 10 H),

1.87-2.03 (m, 8 H), 1.06-1.20 (m, 20 H), 0.72-0.89 (m, 52 H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.40, 151.81, 151.78, 151.42, 147.99, 147.13, 140.45, 140.42, 140.36, 140.19, 140.07, 140.03, 139.90, 139.61, 135.95, 129.16, 126.09, 126.02, 123.83, 123.49, 122.49, 121.43, 121.32, 121.19, 120.38, 119.97, 119.39, 119.35, 55.26, 55.09, 40.25, 40.01, 26.11, 23.11, 23.02, 13.91, 13.85. HRMS (MALDI-TOF) calcd. for $\text{C}_{129}\text{H}_{140}\text{N}_2$: 1718.1045; Found: 1718.1071. Anal. calc. For $\text{C}_{129}\text{H}_{140}\text{N}_2$: C 90.16, H 8.21, N 1.63; found: C 90.14, H 8.22, N 1.60.

(Ph)-OF(2)-NPh. A mixture of 2-bromo-7-diphenylamino-9,9-diphenylfluorene, **6** (452 mg, 0.8 mmol), 7-diphenyl-amino-9,9-diphenylfluorenyl-2-boronic acid, **7** (517.0 mg, 1.0 mmol), 1:2 palladium (II) acetate:tri(*o*-toyl)phosphine (5 mole %), toluene (20 mL), methanol (10 mL) and 2 M K_2CO_3 (2 mL) was heated at 75 °C for overnight. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was further purified by silica gel column chromatography using 2:1 petroleum ether:dichloromethane as eluent. The product was a light yellow solid with an isolated yield of 71 %. ^1H NMR (400 MHz, CDCl_3 , δ) 7.64 (d, $J = 8.40$ Hz, 2 H), 7.55 (d, $J = 8.00$ Hz, 2 H), 7.48-7.50 (m, 4 H), 7.13-7.20 (m, 30 H), 7.02-7.04 (m, 8 H), 6.94-6.99 (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3 , δ) 152.7, 151.3, 147.6, 147.5, 145.8, 139.9, 139.1, 134.2, 129.1, 128.2, 126.6, 126.5, 124.7, 124.2, 123.0, 122.8, 121.5, 120.7, 119.7, 65.4. MS (FAB) m/z 969.8 (M^+). Anal. Calcd for $\text{C}_{74}\text{H}_{52}\text{N}_2$: C, 91.70; H, 5.41; N, 2.89. Found: C, 91.77; H, 5.50; N, 3.06.

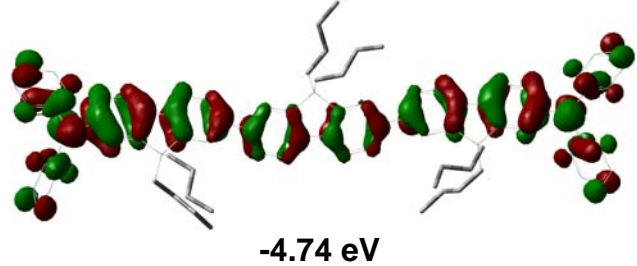
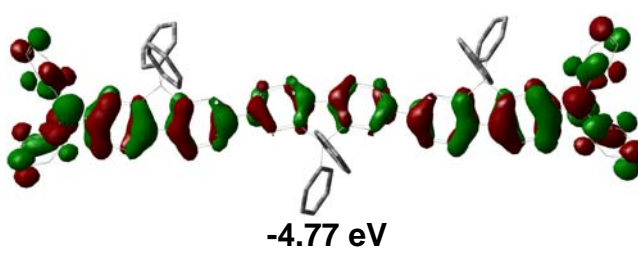
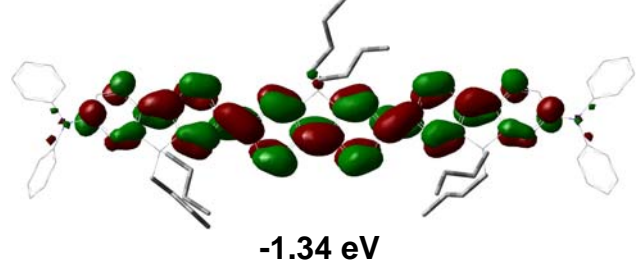
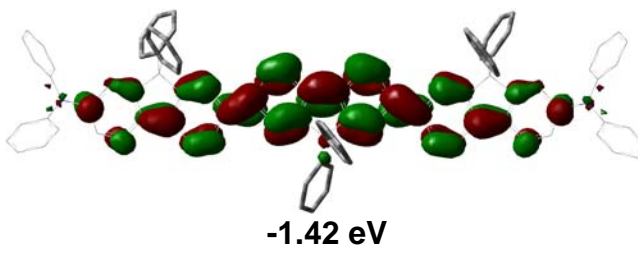
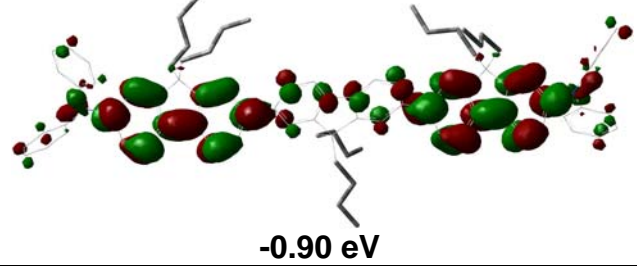
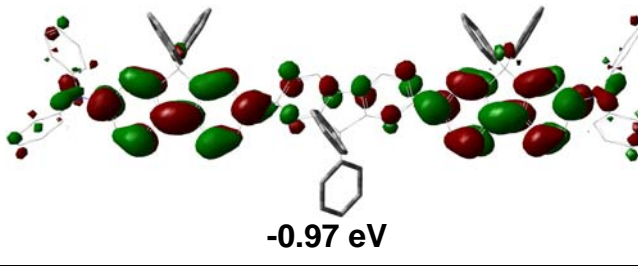
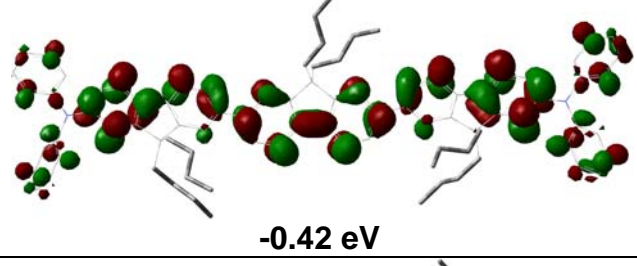
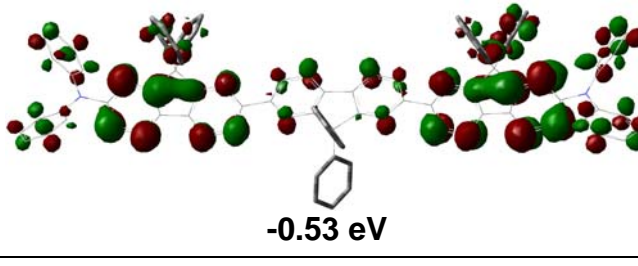
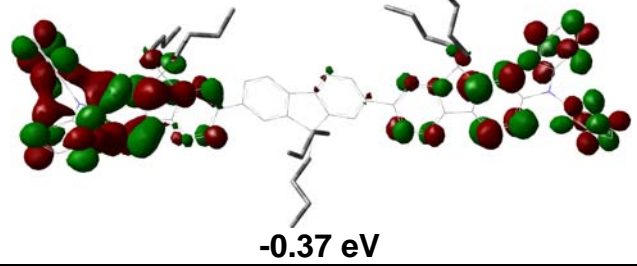
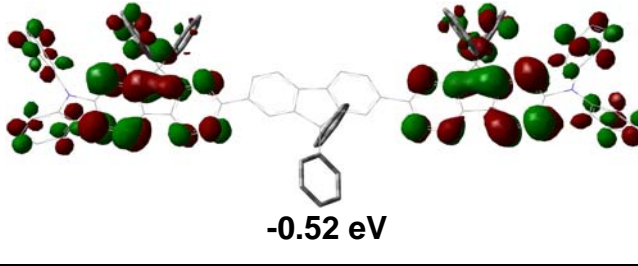
(Ph)-OF(4)-NPh. A mixture of 7,7'-diiodo-2,2'-bi(9,9-diphenylfluorene) **8a** (443 mg, 0.50 mmol), 7-(diphenylamino)-9,9-diphenylfluorenyl-2-boronic acid **7** (776 mg, 1.50 mmol), 1:2 palladium (II) acetate:tri(*o*-toyl)phosphine (5 mole %), toluene (30 mL), methanol (15 mL) and 2 M K_2CO_3 (4 mL) was heated at 75 °C for overnight. After the reaction mixture was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL).

The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The pure product was separated by silica gel column chromatography using 2:1 CH₂Cl₂: petroleum ether as eluent affording 649 mg (81%) of a light-yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 7.74 (d, *J* = 8.00 Hz, 4 H), 7.65 (d, *J* = 8.40 Hz, 2 H), 7.49-7.57 (m, 12 H), 7.13-7.24 (m, 50 H), 7.02-7.05 (m, 10 H), 6.94-6.99 (m, 6 H). MS (FAB) *m/z* 1601.9 (M⁺). Anal. Calcd for C₁₂₄H₈₄N₂: C, 92.97; H, 5.29; N, 1.75. Found: C, 92.73; H, 5.27; N, 1.67.

(Ph)-OF(5)-NPh. The Suzuki cross-coupling procedure for the preparation of **(Ph)-OF(4)-NPh** was followed using 7-(diphenylamino)-9,9-diphenyl-2-boronic acid **7** (150 mg, 0.30 mmol) and 7,7''-diiodo-2,2''-ter(9,9-diphenylfluorene) **8b** (120 mg, 0.10 mmol). The pure product was separated by silica gel column chromatography using 2:1 CH₂Cl₂:petroleum ether as eluent affording 163 mg (84%) of a light-yellow solid. ¹H NMR (400 MHz, CDCl₃, δ) 7.74 (d, *J* = 7.60 Hz, 6 H), 7.65 (d, *J* = 8.80 Hz, 2 H), 7.49-7.57 (m, 16 H), 7.17-7.21 (m, 64 H), 7.03 (d, *J* = 8.00 Hz, 8 H), 6.94-6.96 (m, 6 H). MS (FAB) *m/z* 1918.1 (M⁺). Anal. Calcd for C₁₄₉H₁₀₀N₂: C, 93.29; H, 5.25; N, 1.46. Found: C, 93.12; H, 5.43; N, 1.62.

3. Results of B3LYP/6-31G* calculations³

Calculated spatial distributions of selected frontier molecular orbitals of *(Ph)*-OF(3)-NPh and *(Bu)*-OF(3)-NPh, and their energy levels obtained by B3LYP/6-31G* calculations.

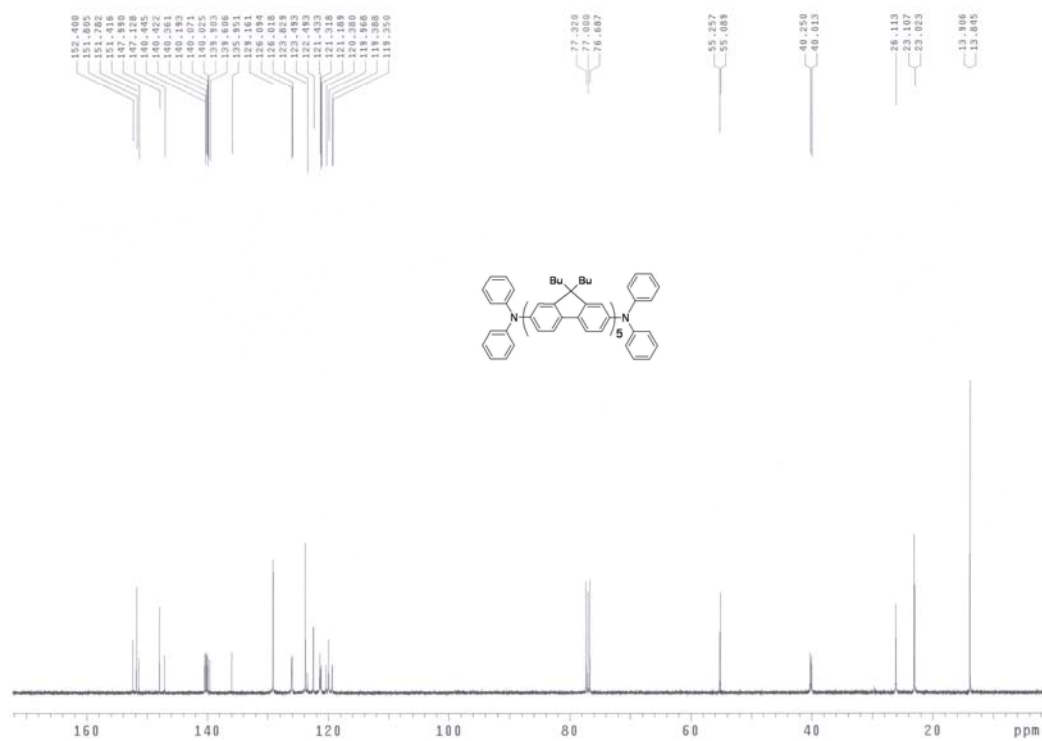
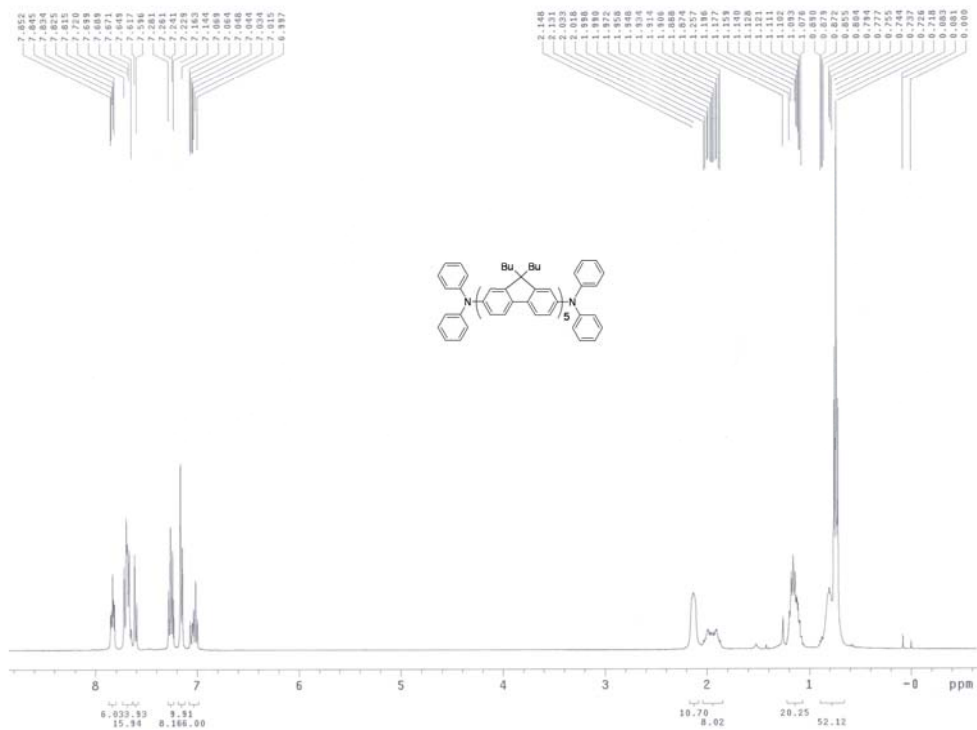
FMOs	FMO of <i>(Bu)</i> -OF(3)-NPh and Energy level	FMO of <i>(Ph)</i> -OF(3)-NPh and Energy level
HOMO	 -4.74 eV	 -4.77 eV
LUMO	 -1.34 eV	 -1.42 eV
LUMO+1	 -0.90 eV	 -0.97 eV
LUMO+2	 -0.42 eV	 -0.53 eV
LUMO+3	 -0.37 eV	 -0.52 eV

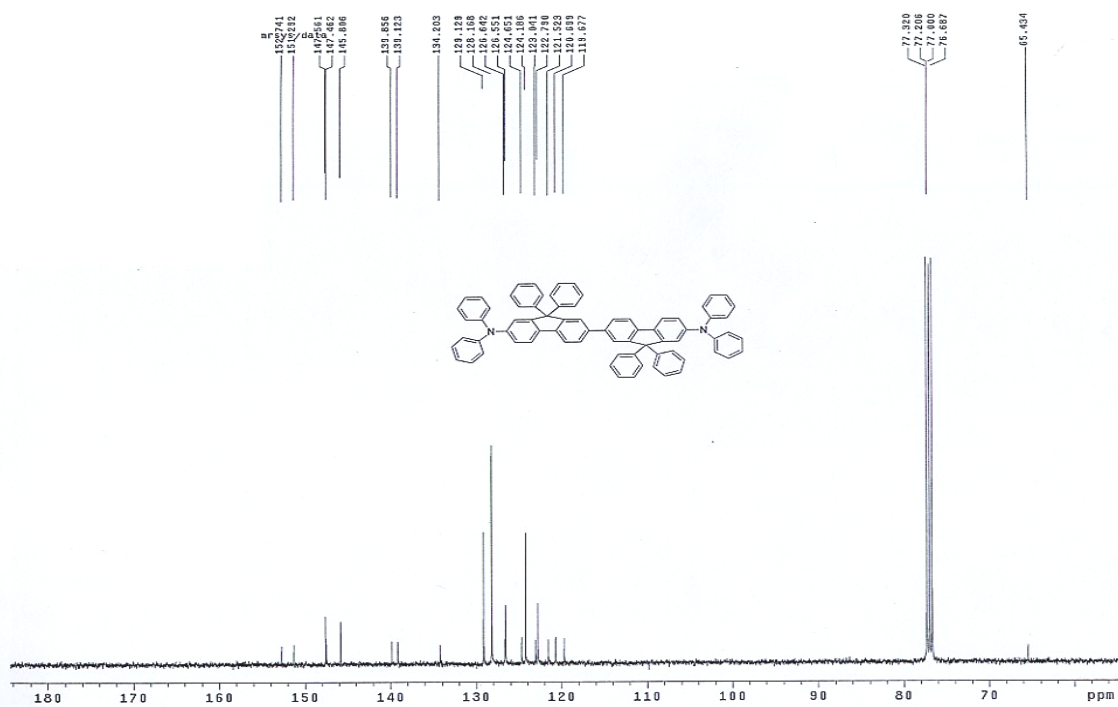
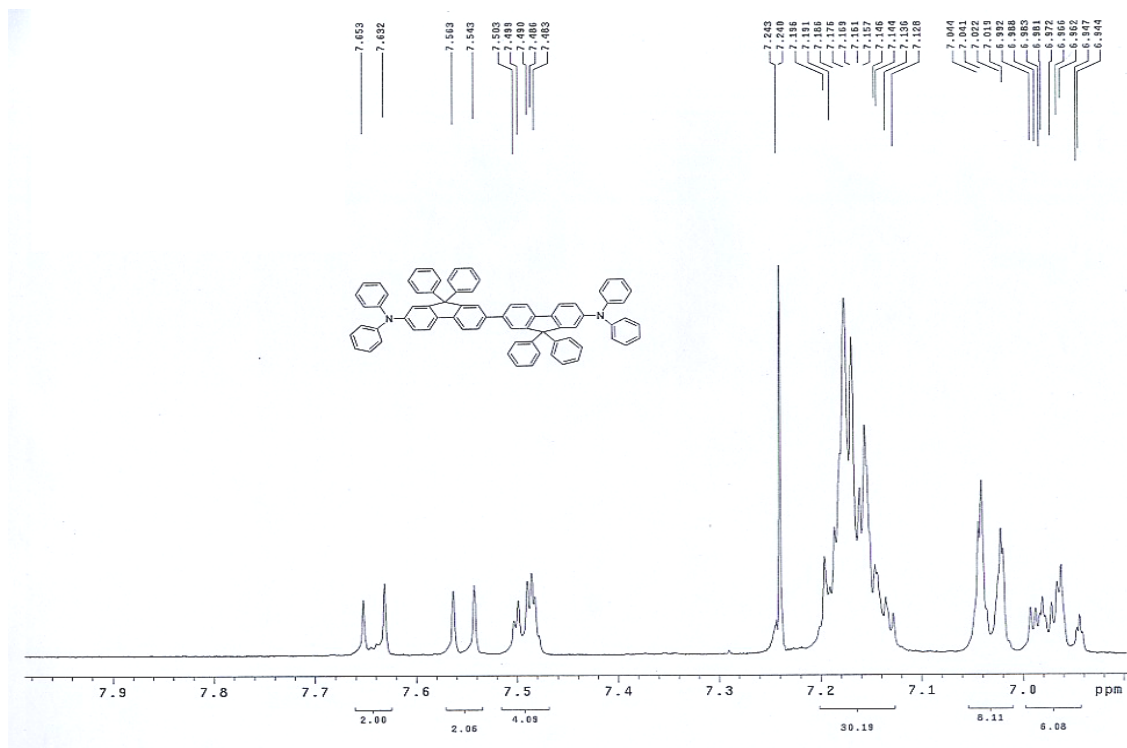
Generally, the molecular orbital coefficients, c_i of molecular orbitals (MOs) can be used to evaluate the contributions of related atomic orbitals (AOs) to these MOs. We have calculated the values of $\sum c_i^2$ of the two substituents, 9,9-diphenyl and 9,9-dibutyl groups, respectively, which can be used to evaluate the contributions of related AOs of the two substituents to the corresponding MOs.

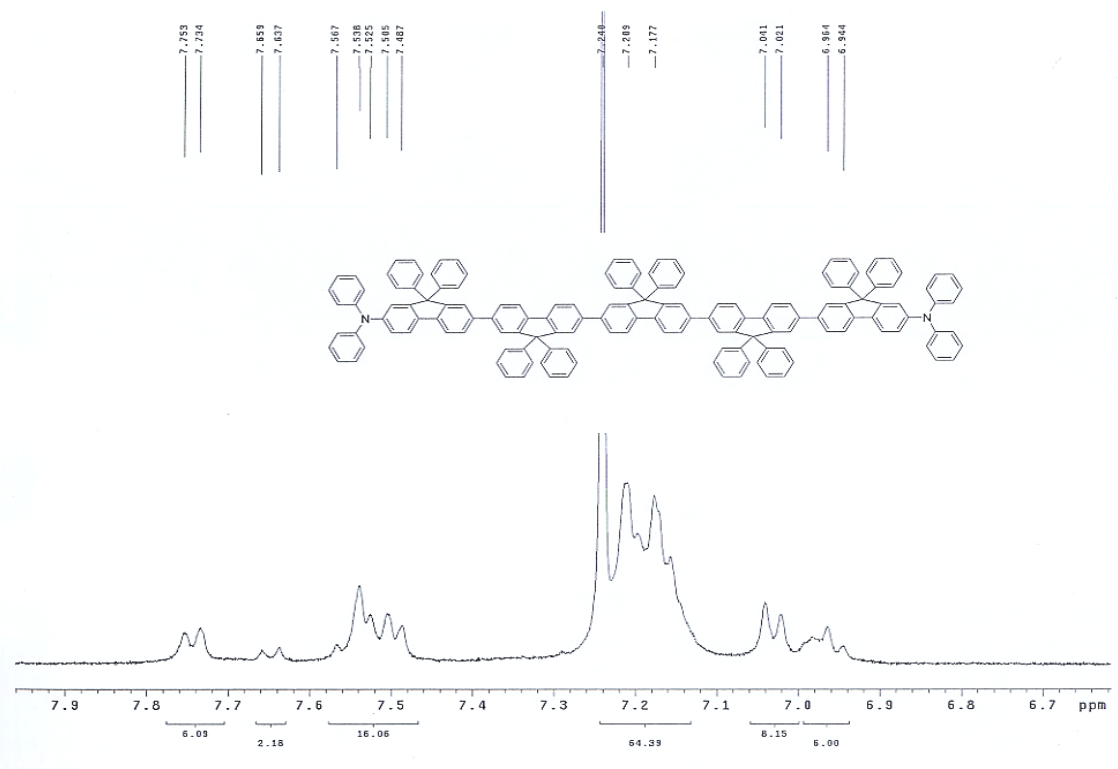
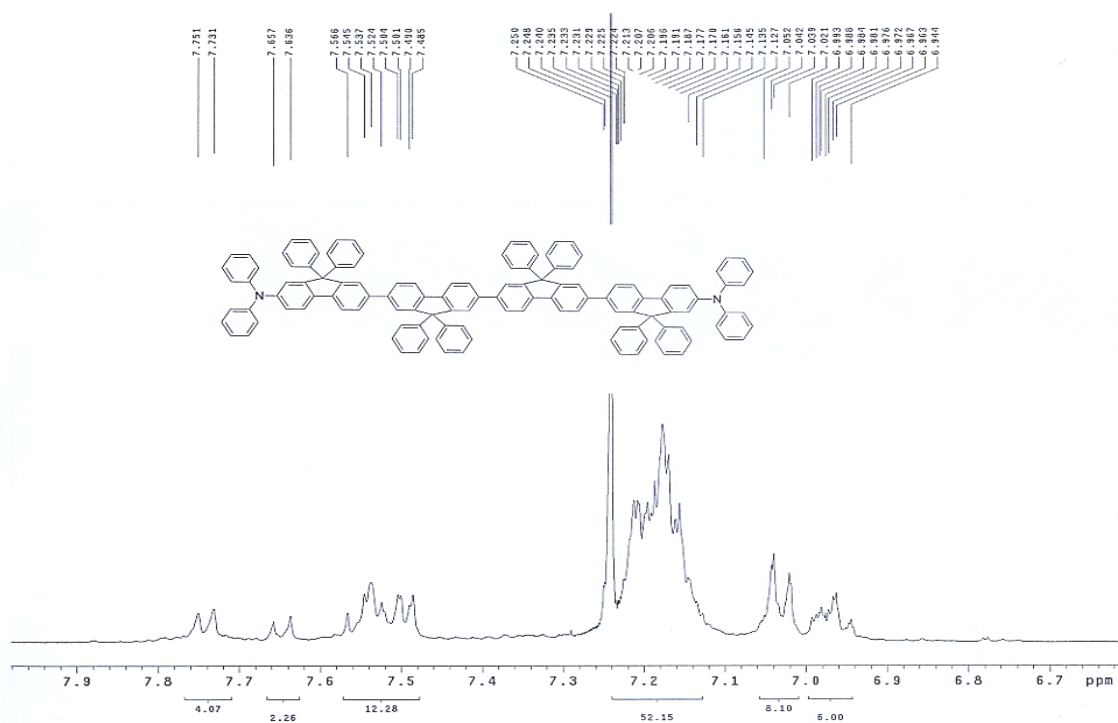
The results of $\sum c_i^2$ show that the relative contributions of the related AOs of 9,9-diphenyl groups to the HOMO, LUMO and LUMO + i ($i = 1, 2, 3, 4$) of (*Ph*)-OF(3)-NPh are 0.0043, 0.0519, 0.0601, 0.2877, 0.3185, and 0.1633, respectively. All of these are larger to a different extent than those of 9,9-dibutyl groups to the HOMO, LUMO and LUMO + i ($i = 1, 2, 3, 4$) of (*Bu*)-OF(3)-NPh, 0.0012, 0.0351, 0.0250, 0.0376, 0.0946, and 0.0907, respectively.

In brief, the greater the contributions of the related atomic orbitals of 9,9-diphenyl groups to the frontier orbitals of (*Ph*)-OF(3)-NPh, the lower the energies of these MOs, and the more stable these MOs are.

4. The ^1H NMR and ^{13}C NMR spectra







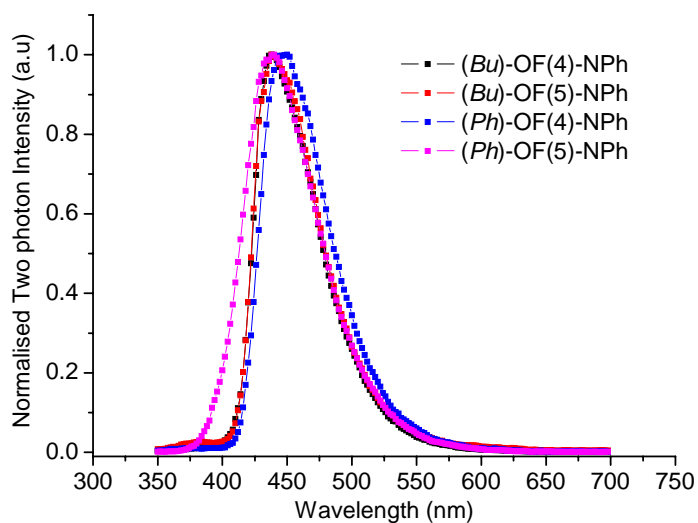


Figure 1 Two-photon excited photoluminescence spectra of **(Bu)-OF(n)-NPh** and **(Ph)-OF(n)-NPh**.

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