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Synthesis and Structure–Property Relationships of Symmetric Ambipolar Quaterfluorene-Containing Oxadiazole as a Central Core and Diphenylamine as End-capping Moieties

Fan Yang,[A] *Xiao Ling Zhang,*[A] *Mo Jun Xiong,*[B] *Zi Jian Cao,*[A] *Ping Fang Xia,*[A]
and Zhong Hui Li[A,C]

[A]Sichuan College of Education, Chengdu, 610041, Sichuan Province, China.
[B]West China School of Pharmacy, Sichuan University, Chengdu,
610041, Sichuan Province, China.
[C]Corresponding author. Email: zhonghli@sohu.com

A facile approach for the synthesis of the symmetric ambipolar quaterfluorene, OF(4)OX-NPh, with hole-transporting and electron-transporting moieties by Suzuki cross-coupling as a key reaction has been developed. This novel ambipolar quaterfluorene exhibits high thermal and electrochemical stabilities and is expected to possess potential application as a double charge-transfer and light-emitting material in the field of single-layer organic emitting diodes.

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Introduction

Highly electron-rich triarylamines known to have a high hole-transporting mobility and to form stable cation radicals have been widely used as hole-transporting materials in light-emitting diodes (LEDs)[1] and shown potential as molecular magnets.[2] It has been shown that light-emitting polymers grafted or end-capped with triarylamine moieties exhibit improved LED device performance.[3] Furthermore, highly electron-deficient oxadiazole (OXA) derivatives have been extensively used as electron-transporting materials as they have efficient electron-transport and hole-blocking characteristics and a high stability to high current density in organic LEDs (OLEDs) devices.[4] However, monodisperse oligofluorenes (OFs) have recently attracted much attention because of their chemical and thermal stabilities and the possibility to vary the functional properties of the resulting compounds via the substitution pattern on the C9 position of the fluorenyl unit, as well as potential applications for optoelectronic molecular materials, especially for OLED devices.[5] Recently, we also found that the incorporation of triarylamines onto the backbone of oligophenylenes (OPPs)[6] and OFs[7] could improve the functional properties of the resulting molecules and device performance of the resulting molecular material-based OLEDs. In particular, we successfully incorporated the hole-transporting triphenylamine unit and electron-transporting oligothienyl moiety into one molecule to afford ambipolar diphenylamino-end-capped oligofluorenylthiophenes as highly efficient hole-transporting ambipolar emitters for OLEDs.[8] In the field of single-layer OLEDs, researchers mainly focus on combining the three components of hole transporting, electron transporting and light-emitting into one molecule to simplify device fabrication and to improve the performance of resulting devices.[9] We herein report the synthesis and functional properties of the novel symmetric ambipolar quaterfluorene OF(4)OX-NPh, in which the hole-transporting, electron-transporting, and emitting moieties are integrated into a single molecule; this molecule has the electronic nature of D-π-A-π-D, which is expected to show novel properties and could be used in fabricating single-layer OLEDs. Furthermore, to compare and to investigate the structure–property relationships of this series of compounds, the functional properties of other quaterfluorene analogues, i.e. OF(4), OF(4)-NPh, and OF(4)OX, are also shown here (Fig. 1).

Results and Discussion

The strategy for preparation of triphenylamine- and oxadiazole-based symmetric ambipolar quaterfluorene OF(4)OX-NPh is outlined in Scheme 1. Monobromination of the 9,9-di(*n*-butyl)fluorene[7a] afforded the corresponding 2-bromo-9,9-di(*n*-butyl)fluorene in an excellent yield of 98% by controlling

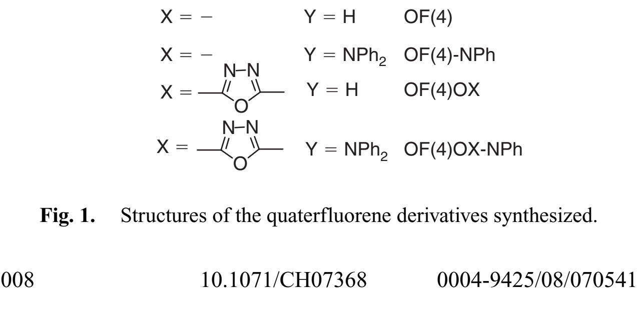

Fig. 1. Structures of the quaterfluorene derivatives synthesized.

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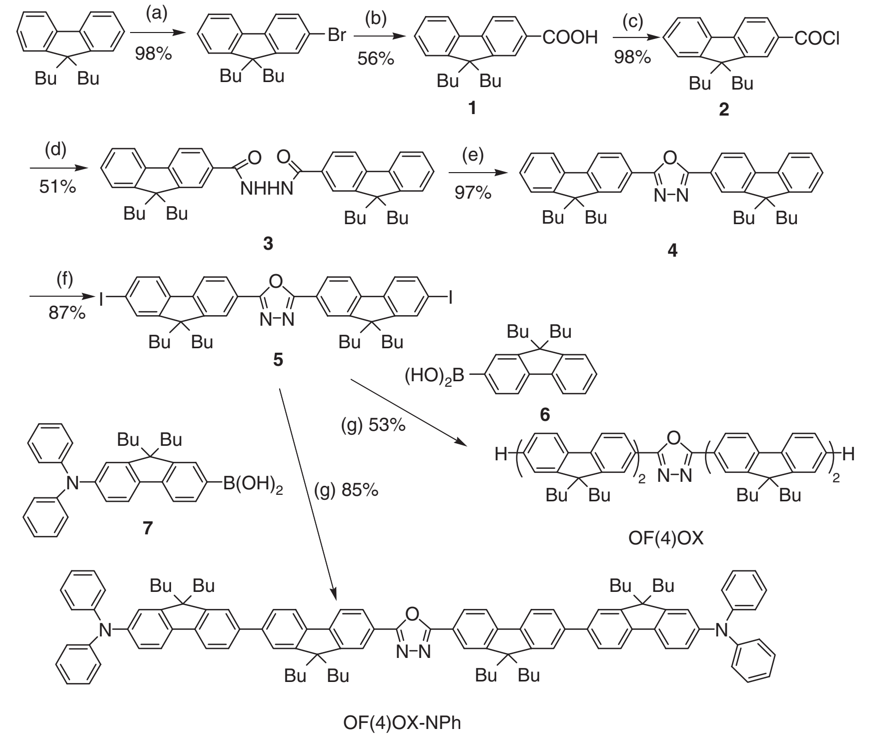

Scheme 1. Synthetic routes of symmetric ambipolar quaterfluorene OF(4)OX-NPh. Reagents and conditions: (a) *N*-bromosuccinimide, acetone, 80°C, overnight. (b) (i) 1.2 equiv. *n*-BuLi, THF, −78°C, 1 h; (ii) dry ice, −78°C–room temp., 2 h. (c) $SOCl_2$, reflux, 4 h. (d) 0.5 equiv. $H_2NNH_2{\cdot}H_2O$, pyridine, $CHCl_3$, 0°C–room temp., overnight. (e) $SOCl_2$, reflux, 4 h. (f) I_2, HIO_4, H_2SO_4–HOAc, 50°C, overnight. (g) 5 mol-% $Pd(OAc)_2$:2P(*o*-tolyl)$_3$, 2 M K_2CO_3, toluene/methanol, N_2, 75°C, overnight.

the total amount of *N*-bromosuccinimide (NBS) and refluxing in acetone solution. Transformation of 2-bromo-9,9-di(*n*-butyl)fluorene into 9,9-di(*n*-butyl)fluorenyl-2-carboxylic acid **1** was carried out in a moderate yield of 56% by lithium–bromine exchange at low temperature, followed by reaction with dry ice at room temperature and subsequently acid hydrolysis. Transformation of the carboxylic acid **1** into the corresponding carbonyl chloride **2** was carried out in an excellent yield of 98% by refluxing a mixture of **1** and an excess of thionyl chloride ($SOCl_2$). Condensation of two equivalents of carbonyl chloride **2** with one equivalent of hydrazine monohydrate ($NH_2NH_2{\cdot}H_2O$) in the presence of a catalytic quantity of pyridine or triethylamine at room temperature afforded the disubstituted hydrazine **3** in a moderate yield of 51%. Then, intramolecular dehydration of disubstituted hydrazine **3** in the presence of $SOCl_2$ afforded 2,5-bis[9′,9′-bis(*n*-butyl)fluorenyl]-1,3,4-oxadiazole **4** in an excellent yield of 98%. Double-iodination of **4** by I_2/HIO_4 gave the corresponding diiodide **5** in a good yield of 87%. Suzuki cross-coupling between the diiodide **5** and 7-diphenylamino-9,9-di(*n*-butyl)fluorenyl-2-boronic acid **7**[7a] using $Pd(OAc)_2$:2P(*o*-tolyl)$_3$ as a catalyst afforded the desired quarterfluorene derivative OF(4)OX-NPh in a good yield of 85%. OF(4)OX was also prepared in a moderate yield of 53% by a similar Suzuki cross-coupling between diiodide **5** and 9,9-di(*n*-butyl)fluorenyl-2-boronic acid **6**[7a] as in the synthetic procedure for OF(4)OX-NPh. The newly synthesized quaterfluorene derivatives OF(4)OX and OF(4)OX-NPh were fully characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis and found to be in good agreement with their structures. Furthermore, the quaterfluorene derivatives without oxadiazole or triphenylamine moieties, OF(4) and OF(4)-NPh, were also synthesized according to our published procedures[7a] for comparison.

The decomposition temperatures (T_{dec}) of quaterfluorene derivatives OF(4), OF(4)-NPh, OF(4)OX, and OF(4)OX-NPh are 451, 464, 446, and 389°C, respectively, indicating that all the quaterfluorene derivatives have good thermal stability (Table 1 and Fig. 2). It is worth mentioning that T_{dec} of the diphenylamino end-capped quaterfluorene OF(4)-NPh remarkably improves in comparison with non-end-capped quaterfluorene OF(4); however, the T_{dec} of ambipolar OF(4)OX-NPh is lower than that of OF(4)OX, suggesting the ambipolar formation in one molecule may lower the thermal stability. Although the quaterfluorene derivative without diphenylamino and oxadiazole moieties OF(4) could not form a stable amorphous glass, the quaterfluorene containing the oxadiazole moiety, OF(4)OX, exhibited a high (up to 87°C) glass transition temperature (T_g) and, more importantly, the glass transition temperature of ambipolar quaterfluorene OF(4)OX-NPh, which is derived from the OF(4)OX end-capped by two diphenylamino groups, is up to 135°C. All the above indicates that the incorporation of the oxadiazole moiety onto the backbone of oligofluorene is necessary for the formation of a stable amorphous glass, and the incorporation of diphenylamino groups onto the backbone of oligofluorene can further enhance the glass transition temperature.

In view of electronic absorption spectra, the absorption bands or maxima of diphenylamino double-end-capped ambipolar quaterfluorenes OF(4)OX-NPh and OF(4)-NPh peaked at 393 and 386 nm, and there was a substantial red shift (Δ 25 nm) of the absorption maxima (λ_{max}) on incorporation of strongly electron-donating diphenylamino groups, which is attributed to

Table 1. Summaries of measurements of quaterfluorene derivatives
CV, cyclic voltammetry; Fc, ferrocene; HOMO, highest occupied molecular orbitals

Compounds	λ_{max}^{abs} ^{A} [nm] ($\varepsilon \times 10^4$ [M^{-1} cm^{-1}])	λ_{max}^{em} ^{A,B} [nm]	$\Phi^{A,C}$	$\tau^{A,D}$ [ns]	HOMO^{E} [eV]	$E_{1/2}{}^{E}$ [eV]	$E_g{}^{F}$ [eV]	$T_g{}^{G}$ [°C]	$T_{dec}{}^{H}$ [°C]
OF(4)	361 (8.23)	410	0.93	0.98	5.53	0.73 0.95	3.02	–	451
OF(4)-NPh	386 (14.2)	432	0.94	0.92	5.14	0.34 0.79 0.94	2.76	117	464
OF(4)OX	368 (7.40)	423	0.59	1.79	5.82	0.69 1.02	3.02	87	446
OF(4)OX-NPh	393 (4.93)	472	0.99	1.72	5.17	0.37 0.97	2.82	135	389

^{A}Measured in $CHCl_3$.
^{B}Excited at the absorption maxima.
^{C}Using quinine sulfate monohydrate (Φ_{313} 0.48) as a standard.
^{D}Using nitrogen laser as an excitation source.
$^{E}E_{1/2}$ v. Fc^+/Fc estimated by CV method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and scanning calomel electrode (SCE) as a reference electrode with an agar salt bridge connecting to the oligomer solution. All the potentials were calibrated with ferrocene, $E_{1/2}$ (Fc/Fc^+) = 0.45 V v. SCE.
^{F}Estimated from the edge of electronic absorption spectra.
^{G}Determined by differential scanning calorimeter from remelt after cooling with a heating rate of 10°C min^{-1} under N_2.
^{H}Determined by thermal gravimetric analyzer with a heating rate of 10°C min^{-1} under N_2.

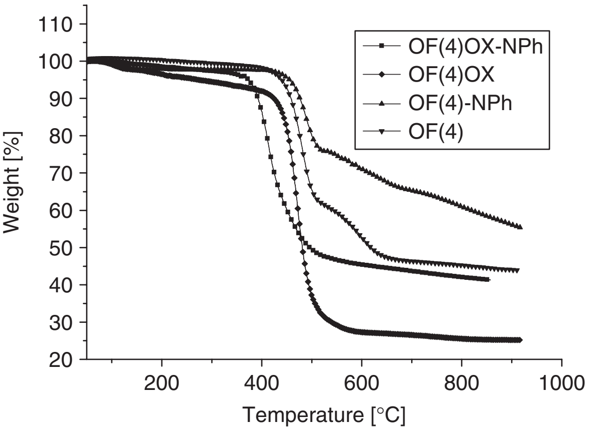

Fig. 2. Thermal gravimetric analysis curves of quaterfluorene derivatives.

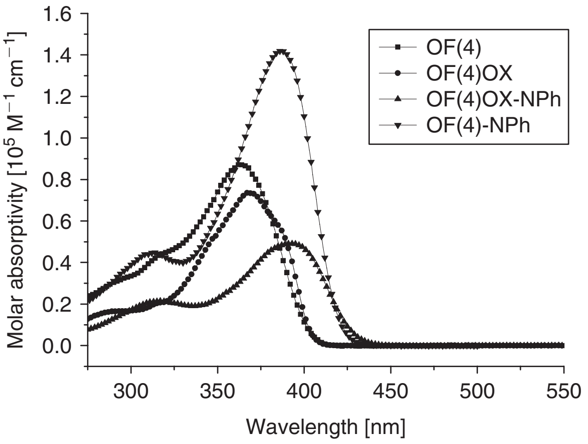

Fig. 3. Absorption spectra of quaterfluorene derivatives, measured in $CHCl_3$.

the asymmetric destabilization of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital levels leading to a decrease in the energy gap[10] (Fig. 3 and Table 1); however, the incorporation of an oxadiazole unit onto the backbone of oligofluorene causes the resulting molecule to be more planar than the analogue without the oxadiazole unit in its electronic ground state, leading to a slightly red-shifted λ_{max}^{abs}.[7a,10] The emission spectra of both non-end-capped quaterfluorenes OF(4) and OF(4)OX have two peaks, at 410 and 430, and at 401 and 423 nm, respectively; however, the emission spectra of diphenylamino-end-capped quaterfluorenes OF(4)OX-NPh and OF(4)-NPh have only one peak at 472 and 432 nm, respectively, and show a significantly red shift (Δ 22–50 nm) in λ_{max}^{em} relative to that of the corresponding OF(4)OX and OF(4) (Fig. 4 and Table 1). This indicates that the excitation energy of diphenylamino-end-capped OF(4)OX-NPh and OF(4)-NPh can be efficiently transferred, whereas that of non-end-capped OF(4)OX and OF(4) cannot. On excitation either at 324 nm attributed to the $n \rightarrow \pi^*$ transition of end-capped triarylamine or at 361 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the quaterfluorene core, the emission spectra obtained are identical, suggesting that energy or exciton can efficiently transfer from the end-capped triarylamine to the quaterfluorene core. The fluorescence quantum yields (Φ_{PL}) of OF(4), OF(4)-NPh, OF(4)OX, and OF(4)OX-NPh measured in chloroform using quinine sulfate monohydrate as a standard are 0.93, 0.94, 0.59, and 0.99, respectively,[11] indicating the incorporation of the oxadiazole moiety onto the backbone of quaterfluorene perturbs the coplanarity and reduces the fluorescence quantum yield of the resulting molecule; however, the Φ_{PL} of diphenylamino end-capped quaterfluorene OF(4)OX-NPh is larger than that of the homologue without diphenylamino end-capping. This implies that in the excited state, better or more π-orbital overlap is attained with the incorporation of end-capping diphenylamino groups onto the backbone of quaterfluorene. However, the emission spectrum of diphenylamino

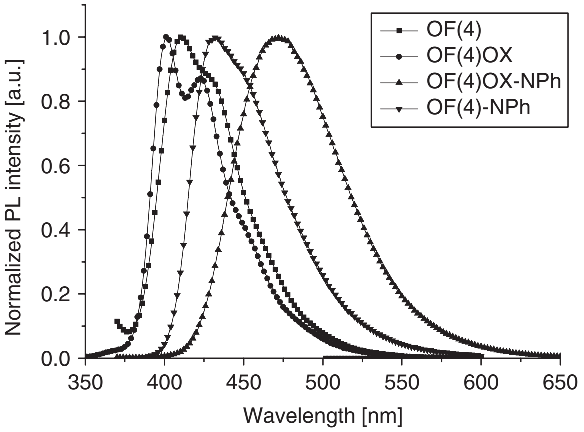

Fig. 4. Emission spectra of quaterfluorene derivatives, measured in $CHCl_3$.

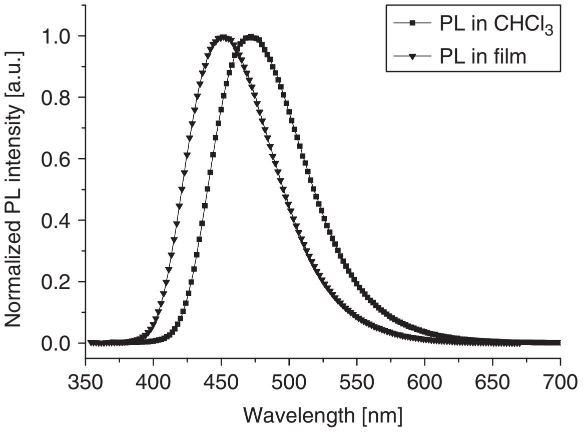

Fig. 5. Emission spectra of diphenylamino-end-capped quaterfluorene OF(4)OX-NPh measured in $CHCl_3$ and as a film.

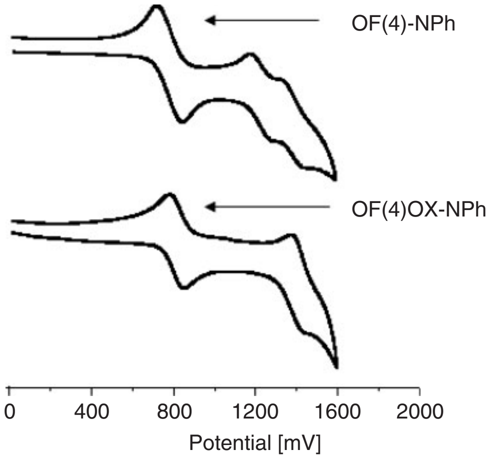

Fig. 6. Cyclic voltammograms of OF(4)OX-NPh and OF(4)-NPh, measured in CH_2Cl_2 using a platinum disc electrode as a working electrode, platinum wire as a counter electrode, and scanning calomel electrode as a reference electrode.

end-capped quaterfluorene OF(4)OX-NPh in a solid film is 452 nm, which blue-shifts ~20 nm relative to its value in chloroform solution (Fig. 5). Furthermore, the fluorescence life-times of all quaterfluorenes are in the nanosecond time-scale, suggesting the emission originates from the singlet excited state to ground state transition.

The electrochemical behaviours of these quaterfluorene derivatives are tabulated in Table 1 and Fig. 6. The ambipolar quaterfluorene OF(4)OX-NPh exhibits similar electrochemical behaviour to the triphenylamine-based oligomers,[6,7] with one reversible two-electron anodic redox couple ($E_{1/2}$ ~0.37 eV) that corresponds to removal of electrons from the end-capped arylamino group of the ambipolar molecule, and another irreversible one-electron anodic redox couple ($E_{1/2}$ ~0.97 eV) that corresponds to removal of electrons from the oligofluorene core containing oxadiazole, forming radical bis-cations and a single cation, respectively (Fig. 6). The similar oxidation potentials of the quaterfluorene backbones of OF(4), OF(4)-NPh, OF(4)OX, and OF(4)OX-NPh are 0.95, 0.94, 1.02, and 0.97 eV, respectively, suggesting they are almost unaffected by the structures of the oligofluorene cores. Furthermore, the first oxidation potential values ($E_{1/2}$: 0.37 and 0.34 eV) of OF(4)OX-NPh and OF(4)-NPh are much smaller than those of the corresponding non-end-capped OF(4)OX ($E_{1/2} = 1.02$ eV) and OF(4) ($E_{1/2} = 0.73$ eV) (Table 1), indicating that incorporation of diphenylamino groups onto the quaterfluorene backbone makes the resulting molecule more stable to electrochemical oxidation. In general, owing to the easy oxidation of triarylamine to form relatively more stable radical dications, with the incorporation of triarylamine, the HOMO energy level of oligofluorenes moves up to ~5.15 eV (relative to the vacuum level) as estimated by the electrochemical method. Such a high HOMO energy level greatly reduces the energy barrier for the hole injection from indium tin oxide (quantum yield (ϕ) = 5.0 eV) to the emissive oligofluorenes. As a result, OF(4)OX-NPh and OF(4)-NPh can also be used as hole transport or injection materials.

Conclusions

A facile approach for synthesis of the symmetric ambipolar oligofluorene-containing hole-transporting and electron-transporting moieties by Suzuki cross-coupling as a key reaction has been presented. This approach will be applicable for the construction of other structurally uniform and well-defined π-conjugated functional ambipolar oligomers. All the quaterfluorene compounds were characterized by a combination of ^1H and ^{13}C NMR spectroscopy and elemental analysis. The newly synthesized symmetric ambipolar oligofluorene OF(4)OX-NPh exhibits good thermal and electrochemical stabilities. The details of the OLED performance using this material as a charge transfer and emitting layer will be reported in the future.

Experimental

General Procedures and Requirements

All the solvents were dried by the standard methods wherever needed. ^1H NMR spectra were recorded using either a JEOL JHM-EX270 FT NMR spectrometer or a Varian INOVA-400 FT NMR spectrometer and are referenced to residual $CHCl_3$ (7.24 ppm) or DMSO (2.5 ppm). ^{13}C NMR spectra were recorded using a Varian INOVA-400 FT NMR spectrometer and are referenced to $CDCl_3$ (77 ppm) or $[D_6]DMSO$ (39.5 ppm). Mass spectroscopy (MS) measurements were carried out using fast atom bombardment (FAB) on an API ASTAR Pulsar I Hybrid mass spectrometer. Elemental analysis was carried on a CARLO ERBA 1106 Elemental Analyzer. Thermal stabilities were determined with a thermal gravimetric analyzer (PE-TGA6) with a heating rate of 10°C min^{-1} under N_2. Glass transitions and melting transitions were extracted from the second-run differential scanning calorimetry (DSC) traces, which were determined with a DSC (PE Pyris Diamond DSC) with a heating rate of 10°C min^{-1} under N_2. All the physical measurements were performed in $CHCl_3$ including electronic absorption (UV-visible) and fluorescence spectra. Electronic absorption (UV-visible) and fluorescence spectra were recorded using a Varian Cary 100 Scan Spectrophotometer and a PTI luminescence spectrophotometer, respectively. The fluorescence quantum yields in chloroform were determined by the dilution method using quinine sulfate monohydrate (λ_{exc} 313 nm, Φ 0.48) as a standard. The fluorescence decay curves were recorded at room temperature using a nitrogen laser for excitation. The lifetimes were estimated from the measured fluorescence decay using an iterative fitting procedure. $E_{1/2}$ v. ferrocene $(\mathrm{Fc})^+/\mathrm{Fc}$ was estimated by the cyclic voltammetric method (Voltammetric Analyzer CV-50W) using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and scanning calomel electrode (SCE) as a reference electrode with an agar salt bridge connecting to the oligomer solution dissolved in CH_2Cl_2, using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV s^{-1}, and all the potentials were calibrated with ferrocene ($E_{1/2}$ $(\mathrm{Fc}/\mathrm{Fc}^+) = 0.43$ V v. SCE) as an external standard.

Synthesis

*9,9-Bis(*n*-butyl)fluorene-2-carboxylic Acid **1***

To a 100-mL two-necked flask containing 9,9-bis(*n*-butyl)-2-bromofluorene (3.80 g, 10.60 mmol) in 20 mL dried THF equipped with a magnetic stirrer was added dropwise 1.5 M *n*-butyl lithium (8.5 mL, 12.73 mmol) under a nitrogen atmosphere with a −78°C acetone–dry ice bath while maintaining good stirring. After stirring for 1 h, dry ice (0.70 g, excess) was added. After stirring for another 2 h, water was added to the reaction mixture, and then HCl (6 M) was added in a dropwise fashion until an acidic solution was obtained. The reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was then purified by silica gel column chromatography using petroleum spirits/EtOAc as gradient eluent, affording the desired carboxylic acid as a white solid (1.08 g, 56%). δ_H (400 MHz, $CDCl_3$) 8.14 (dd, *J* 8.0, 1H), 8.09 (s, 1H), 7.79–7.76 (m, 2H), 7.38–7.35 (m, 3H), 2.08–1.97 (m, 4H), 1.11–1.02 (m, 4H), 0.67–0.59 (t, *J* 7.4, 6H), 0.57–0.51 (m, 4H). δ_H (400 MHz, [D_6]DMSO) 12.91 (s, 1H), 7.94 (s, 4H), 7.48 (s, 1H), 7.38 (s, 2H), 2.01 (s, 4H), 1.00 (s, 4H), 0.60 (s, 6H), 0.43 (s, 4H). δ_C (100 MHz, $CDCl_3$) 172.7, 151.9, 150.8, 146.8, 139.7, 129.6, 128.5, 127.6, 127.0, 124.6, 123.1, 120.7, 119.5, 55.2, 40.0, 25.9, 23.0, 13.8. *m/z* (FAB) 322.5 [M^+].

*9,9-Bis(*n*-butyl)fluorene-2-carbonyl Chloride **2***

After refluxing a mixture of 9,9-bis(*n*-butyl) fluorene-2-carboxylic acid **1** (1.80 g, 5.60 mmol) and thionyl chloride ($SOCl_2$, 10 mL) for 2 h, the excess thionyl chloride was removed by simple distillation. Benzene (80 mL) was added to the reaction mixture and then was distilled out by simple distillation to remove the by-product sulfite acid (H_2SO_3), affording the colourless liquid residue product with an isolated yield of 98% (1.91 g). δ_H (400 MHz, $CDCl_3$) 8.15 (dd, *J* 8.1, 1H), 8.03 (d, *J* 1.6, 1H), 7.78 (d, *J* 8.4, 2H), 7.41–7.34 (m, 3H), 2.04–1.98 (m, 4H), 1.11–1.00 (m, 4H), 0.65 (t, *J* 7.3, 6H), 0.60–0.51 (m, 4H). δ_C (100 MHz, $CDCl_3$) 168.3, 152.2, 151.2, 148.4, 138.9, 131.5, 131.3, 129.2, 127.2, 125.5, 123.1, 121.1, 119.7, 55.4, 39.9, 26.0, 23.0, 13.8. *m/z* (FAB) 340.5 [M^+].

*1,2-Bis[9′,9′-bis(*n*-butyl)fluorene-2′-carbonyl] Hydrazine **3***

To a mixture of 9,9-bis(*n*-butyl)fluorene-2-carbonyl chloride **2** (1.91 g, 5.6 mmol), pyridine (475 mg, 5.6 mmol) and chloroform (30 mL) was added dropwise a solution of hydrazine ($H_2NNH_2 \cdot H_2O$, 127 mg, 2.6 mmol) in chloroform (20 mL) in an ice–water bath while maintaining good magnetic stirring. After completion of the addition, the reaction mixture was stirred for another 4 h at room temperature. The reaction mixture was first poured into water, and then sodium carbonate (2 M) was added in a dropwise fashion until a neutral solution was obtained and the solution extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was then purified by silica gel column chromatography using petroleum spirits/EtOAc as gradient eluent, affording the desired hydrazine **3** as a white solid (830 mg, 51%). δ_H (400 MHz, $CDCl_3$) 9.78 (s, 2H), 7.92 (d, *J* 6.8, 4H), 7.77–7.71 (m, 4H), 7.34 (d, *J* 5.4, 6H), 2.02–1.96 (m, 8H), 1.06–0.98 (m, 8H), 0.63–0.49 (m, 20H). δ_C (100 MHz, $CDCl_3$) 164.4, 151.5, 151.2, 145.5, 139.6, 129.6, 128.2, 126.9, 126.4, 123.0, 121.7, 120.5, 119.8, 55.4, 40.1, 26.0, 23.0, 13.9. *m/z* (FAB) 641.8 [$M^+ + 1$].

*2,5-Bis[9′,9′-bis(*n*-butyl)fluorenyl]-1,3,4-oxadiazole **4***

After a mixture of 1,2-bis[9′,9′-bis(*n*-butyl)fluorene-2′-carbonyl] hydrazine **3** (0.81 g, 1.26 mmol) and thionyl chloride ($SOCl_2$, 10 mL, excess) was refluxed for 4 h, the excess thionyl chloride was removed by simple distillation. The residue mixture was poured into ice–water, and dichloromethane (100 mL) was added to dissolve the solid product, the organic layer was collected and washed with water first, then sodium carbonate (2 M) until a neutral solution was obtained, and lastly water. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness, affording the desired pure oxadiazole derivative **4** as a white solid (766 mg, 97%). δ_H (400 MHz, $CDCl_3$) 8.16–8.12 (m, 4H), 7.86–7.83 (m, 2H), 7.78–7.76 (m, 2H), 7.38–7.37 (m, 6H). δ_C (100 MHz, $CDCl_3$) 165.1, 151.6, 151.4, 144.7, 139.9, 128.3, 127.0, 126.0, 123.0, 122.3, 121.3, 120.4, 120.1, 55.4, 40.1, 25.9, 23.0, 13.8. *m/z* (FAB) 623.7 [$M^+ + 1$]. Calc. for $C_{44}H_{50}N_2O$ C 84.8, H 8.1, N 4.5. Found C 84.9, H 8.2, N 4.5%.

*2,5-Bis[9′,9′-bis(*n*-butyl)-2′-iodofluorenyl]-1,3,4-oxadiazole **5***

A mixture of 2,5-bis[9′,9′-bis(*n*-butyl)fluorenyl]-1,3,4-oxadiazole **4** (512 mg, 0.82 mmol), acetic acid (10 mL), water (1 mL), concentrated sulfuric acid (1 mL), iodine (229 mg, 0.90 mmol), iodic acid (309 mg, 0.90 mmol), and carbon tetrachloride (2 mL) was heated at 50°C overnight with good magnetic stirring. After the product slurry was cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined dark purple organic layers were decolourized with sodium sulfite, washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. Purification of the crude product by silica gel column chromatography using 1:1 petroleum spirits/dichloromethane afforded the *title compound* as a yellow solid with an isolated yield of 87% (624 mg). δ_H (400 MHz, $CDCl_3$) 8.14 (d, *J* 8.4, 8H), 7.81 (d, *J* 8.8, 2H), 7.69 (d, *J* 8.8, 4H), 7.50 (d, *J* 8.4, 2H), 2.10–1.94 (m, 8H), 1.13–1.04 (m, 8H), 0.65 (t, *J* 7.4, 12H), 0.60–0.52 (m, 8H). δ_C (100 MHz, $CDCl_3$) 165.0, 153.6, 151.0, 143.7, 139.5, 136.2, 132.2, 126.1, 122.8, 122.0, 121.3, 120.3, 94.2, 55.6, 40.0, 25.9, 22.9, 13.8. *m/z* (FAB) 875.4 $[M^+ + 1]$.

*2,5-Bis[5′,2″-bi(9′,9′-bis(*n*-butyl)fluorenyl)]-1,3,4-oxadiazole OF(4)OX*

A mixture of 2,5-bis[9′,9′-bis(*n*-butyl)-2′-iodofluorenyl]-1,3,4-oxadiazole **5** (219 mg, 0.25 mmol), palladium(II) acetate (2.8 mg, 0.013 mmol), tri-*o*-tolylphosphine (7.6 mg, 0.026 mmol), 9,9-di(*n*-butyl)fluorenyl-2-boronic acid **6** (242 mg, 0.75 mmol), toluene (10 mL), methanol (5 mL), and 2 M K_2CO_3 (2 mL) was heated at 75°C overnight under a nitrogen atmosphere while maintaining good magnetic stirring. After the reaction mixture cooled to room temperature, it was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography using 1:1 petroleum spirits/dichloromethane as eluent, affording the title compound as a white solid (155 mg, 53%). δ_H (400 MHz, $CDCl_3$) 8.17–8.11 (m, 8H), 7.90–7.83 (m, 4H), 7.78–7.76 (m, 8H), 7.38–7.37 (m, 6H). δ_C (100 MHz, $CDCl_3$) 165.1, 152.3, 151.6, 151.5, 151.4, 148.0, 144.7, 147.2, 144.5, 141.8, 139.9, 139.4, 139.2, 139.0, 135.8, 128.3, 127.0, 126.0, 123.0, 122.3, 121.3, 120.7, 120.4, 120.2, 120.1, 55.4, 55.2, 40.1, 25.9, 23.0, 13.8. *m/z* (FAB) 1176.6 $[M^+ + 1]$. Calc. for $C_{86}H_{98}N_2O$ C 87.9, H 8.4, N 2.4. Found C 87.9, H 8.5, N 2.4%.

*2,5-Bis[5′,2″-bi(2′-diphenylamino-9′,9′-bis(*n*-butyl)fluorenyl)]-1,3,4-oxadiazole OF(4)OX-NPh*

The procedure above was followed using 9,9-di(*n*-butyl)-2-diphenylamino-7-fluorenyl boronic acid **7** (260 mg, 0.53 mmol), 2,5-bis[9′,9′-bis(*n*-butyl)-2′-iodofluorenyl]-1,3,4-oxadiazole **5** (155 mg, 0.18 mmol), palladium(II) acetate (5.6 mg, 0.025 mmol), tri-*o*-tolylphosphine (15 mg, 0.050 mmol), toluene (10 mL), methanol (5 mL), and 2 M K_2CO_3 (2 mL). The crude product was further purified by silica gel column chromatography using 1:2 petroleum spirits/dichloromethane as eluent, affording the title compound as a light-yellow solid (228 mg, 85%). δ_H (400 MHz, $CDCl_3$) 8.17 (d, *J* 7.6, 4H), 7.87 (dd, *J* 8.0, 4H), 7.71–7.58 (m, 12H), 7.25 (t, *J* 8.0, 8H), 7.14–7.12 (m, 10H), 7.05–6.99 (m, 6H), 2.16–2.12 (m, 8H), 1.97–1.89 (m, 8H), 1.16–1.07 (m, 16H), 0.74–0.67 (m, 40H). δ_C (100 MHz, $CDCl_3$) 165.2, 152.4, 152.2, 151.9, 151.5, 148.0, 147.2, 144.5, 141.8, 140.5, 139.2, 139.0, 135.8, 129.2, 126.3, 126.1, 123.9, 123.5, 122.5, 122.3, 121.4, 121.2, 120.7, 120.2, 119.4, 119.3, 55.6, 55.1, 40.2, 40.0, 26.1, 26.0, 23.0, 13.9, 13.8. *m/z* (FAB) 1510.1 $[M^+]$. Calc. for $C_{110}H_{116}N_4O$ C 87.5, H 7.7, N 3.7. Found C 87.3, H 7.6, N 3.7%.

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