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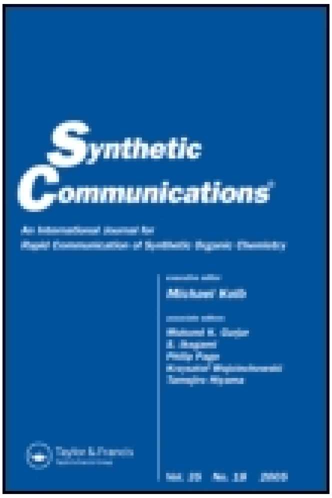

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Synthesis and Characterization of Novel Perylenediimide-Cored Dendrimer with Fluorinated Shell

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SYNTHESIS AND CHARACTERIZATION OF NOVEL PERYLENEDIIMIDE-CORED DENDRIMER WITH FLUORINATED SHELL

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A perylenediimide-based dendrimer, PDI-F, was designed and synthesized for application as red host emitter in nondoped organic light-emitting diodes. PDI-F was designed with perylenediimide as the luminescence core and pentafluorophenyl rings as the surface groups. The dendrimer molecule constructed in this way is bulky and nonplanar. PDI-F exhibits good solubility in common organic solvents and is suitable for wet methods such as spin coating to make thin films. All new compounds of the intermediates and the target dendrimer were characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis. In addition, the ultraviolet (UV) absorption and fluorescence (FL) of PDI-F were measured and discussed. To the best of our knowledge, this is the first report of dendrimer PDI-F.

Keywords: Dendrimer; fluorinated shell; perylenediimide

INTRODUCTION

Organic light-emitting diodes (OLEDs) are attracting more and more research attention because of their practical applications in large-area flat-panel displays and lighting.[1,2] Currently, the red-light-emitting materials and devices still lag behind the green and blue components in both efficiency and stability and require further improvements to match the criteria of full-color displays and white-light lighting.[3] Recently, developing red host emitters for nondoped light-emitting diodes has become a prevalent strategy to gain highly efficient red electroluminescence (EL).[4–9]

In this article, we designed and synthesized a novel red-emitting perylenediimide dendrimer, PDI-F, with pentafluorophenyl peripheral groups (shown in Fig. 1). Perylenediimide was selected as the luminescent core because of its red fluorescence and high fluorescent quantum yield.[10] To prevent intermolecular aggregation and concentration quenching, the bulky dendrons were introduced into all four bay positions of the perylene ring to construct a nonplanar molecule. Pentafluorophenyl rings were grafted to the dendrimer surface to function as the electron-transporting moieties.

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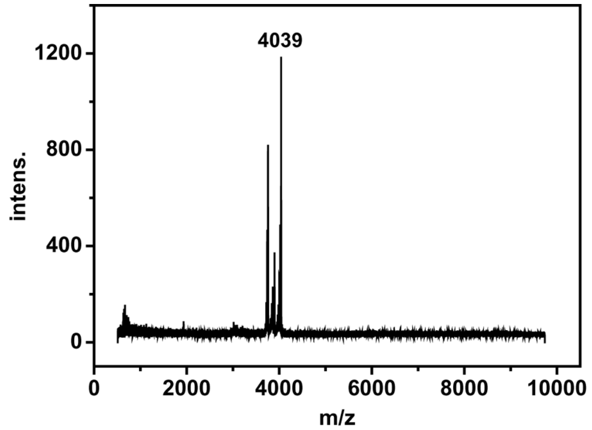


Figure 1. MALDI-TOF-MS (calcd. for $C_{192}H_{58}F_{80}N_2O_8$ as 4038.29).

RESULTS AND DISCUSSION

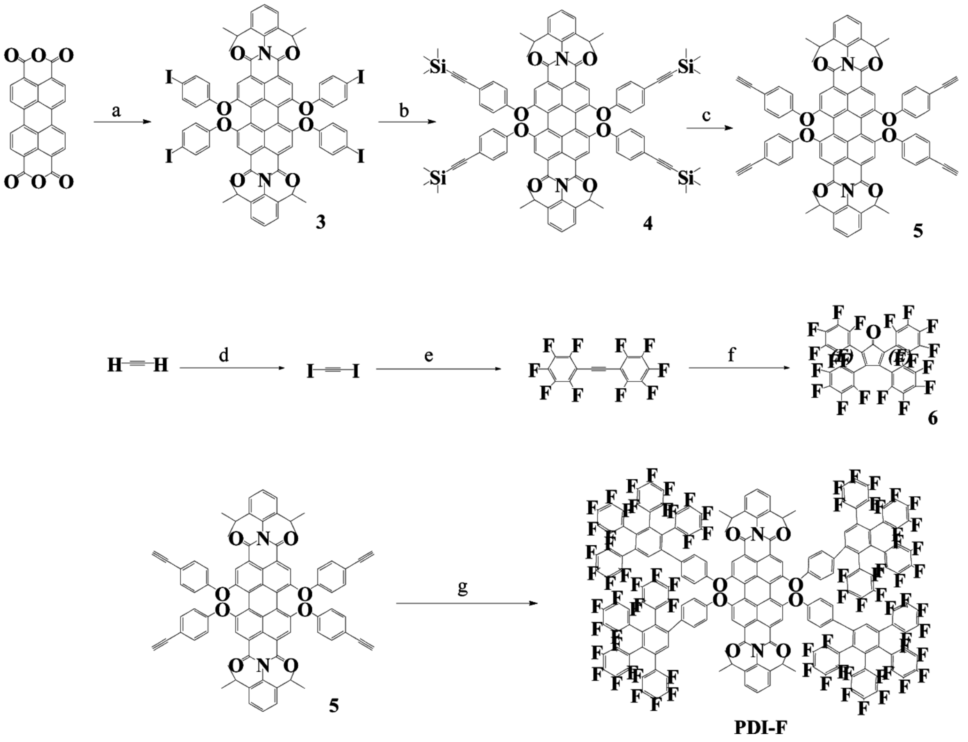
Design and Synthesis

The dendrimer PDI-F was synthesized through the procedure described in Scheme 1. To prevent intermolecular aggregation and concentration quenching, the bulky dendrons were introduced through bisaryl ether structure into all four bay positions of the perylene ring. The pentafluoropheneyl type dendron was formed by Diels–Alder cycloaddition of tetrakis(pentafluoropheneyl)cyclopentadienone **6** to the terminal ethynyl groups on the surface of the perylenediimide-based core **5**. Pentafluorophenyl rings were designed as the surface groups of the dendrimer because of the strong electron-withdrawing nature and potential electron-transporting function.

The perylenediimide-containing core **5**, bearing the light-emitting functional group, and tetrakis(pentafluorophenyl)cyclopentadienone **6**,[11–13] bearing electron-transporting groups, are two important intermediates and were prepared through several step reactions as shown in Scheme 1. The chemical structures of all intermediates were confirmed by ^{1}H NMR and mass spectroscopy. Finally, the cycloaddition of **5** and **6** in *o*-xylene at high temperature generated the target dendrimer PDI-F, which is soluble in normal organic solvents and was purified by flash column chromatograph over silica gel with mixed petroleum ether and dichloromethane (3:2) as eluent. The observation of $[M+H]^+$ peak at ca. m/z 4039 in matrix-assisted laser desorption/ionization time-of-light (MALDI-TOF) mass spectra (shown in Fig. 1) and ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectral data along with elementary analysis unambiguously confirmed the chemical structure of the target dendrimer PDI-F.

Optical Properties

The normalized electronic absorption and fluorescence spectra of PDI-F solution in dichloromethane and film spin coated on quartz substrate are shown in Fig. 2. PDI-F exhibits absorption bands at 560, 523, and 440 nm in both solution and film, which are associated with the π–π^* transition of the perylenediimide



Scheme 1. Synthesis of dendrimer PDI-F. (a) Br_2, H_2SO_4 (98 wt%); 4-iodophenol, NMP, K_2CO_3, 80 °C 15 h, 80%; (b) trimethyl-silylethyne, $[PdCl_2(PPh_3)_2]$, CuI, THF/Et_3N, rt, overnight, 85%; (c) n-Bu_4NF, THF, rt, overnight, 87%; (d) KI, NaClO, aq.; (e) bromopentaflurobenzene, Mg, dry ether, reflux, 30 min, $CoCl_2$, −20 °C, overnight, 45%; (f) $Co_2(CO)_8$, o-xylene, rt, overnight; 195 °C, 48 h, 54%; (g) **6**, o-xylene, reflux, 7 days, 81%.

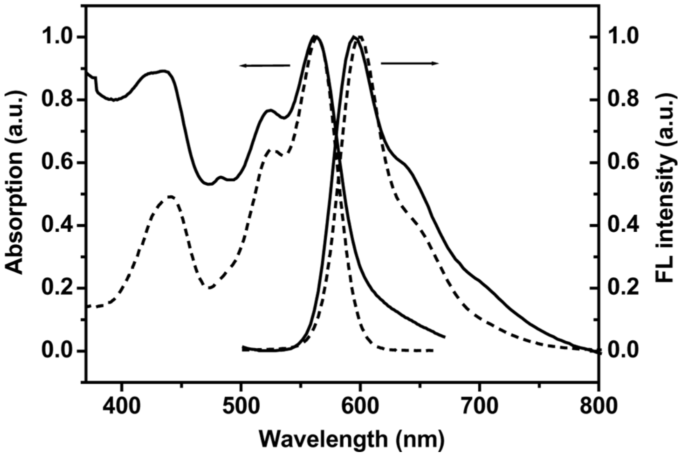


Figure 2. Absorption and fluorescence spectra of PDI-F solutions in dichloromethane and films spin coated on quartz substrates.

core.[13] The pentafluorophenyl peripheral groups are transparent in the visible-light region. Upon photoexcitation at 523 nm, PDI-F exhibits red fluorescence in dichloromethane solution with the emission peak at 605 nm and two shoulders at 640 and 700 nm. The fluorescent quantum yield of PDI-F in dilute ethanol was measured as cal. 0.81 using Rhodamine B in ethanol ($\Phi = 0.90$) as standard. The fluorescence spectrum of PDI-F film has features similar to that of solution, but slightly blue-shifted by 3 nm compared to the solution. Another change is that the emission intensity of 640- and 700-nm bands increased in film, which is favorable for generating saturated red emission. The absence of any long-wavelength emission band excludes the possibility of intermolecular aggregates or excimer formation even in solid film, which should benefit from the hindrance of intermolecular stacking by the nonplanar molecular conformation.

EXPERIMENTAL

Materials and Instruments

All the chemicals for the synthesis are of analytical grade and were used as received without further purification. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Varian Inova spectrometer (400 MHz); chemical shifts were referenced to tetramethylsilane (TMS) and fluorobenzene respectively. Mass spectra (MS) were recorded on a Micromass Q-Tof (Micromass, Wythenshawe, U.K.) mass spectrometer for electrospray ionization (ESI)–MS and a Bruker Biflex III mass spectrometer for MALDI-TOF-MS. Elemental analyses were carried out on a Carlo-Erba 1106 elemental analyzer. Absorption and fluorescence spectra were recorded with a ultraviolet–visible (UV-vis) spectrophotometer (Perkin-Elmer Lambda 35) and a fluorospectrophotometer (Perkin-Elmer Luminescence LS50B), respectively.

Synthesis of Compounds

1,6,7,12-Tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride (1). A mixture of perylene-3,4,9,10-tetracarboxylic acid bisanhydride (10 g, 25 mmol) and 200 mL of 98 wt% sulfuric acid was stirred at room temperature for 12 h. The mixture was then heated to 85 °C, and 0.31 g I_2 (1.2 mmol) was added. Subsequently, 5 mL (15.595 g, 195 mmol) Br_2 was added dropwise over 12 h, and the reaction mixture was heated for 24 h at 85 °C. Then 0.31 g I_2 (1.2 mmol) was added, and the reaction temperature was raised to 110 °C. Five mL (15.595 g, 195 mmol) Br_2 were added dropwise over 12 h, and the reaction mixture was heated for an additional 80 h at 110 °C. After being cooled to room temperature, the excess bromine was removed by saturated solution of $NaHSO_3$. The resultant precipitate was washed with a large amount of water until the filtrate became neutral. The solid residue was dried in a vacuum at 120 °C for 8 h to give 18 g (90%) of a red-brown powder. The crude product was used directly in a later reaction without further purification because of its insolubility in organic solvents.

N′-(2,6-Diisopropylphenyl)-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisimide (2). 2,6-Diisopropylaniline (2.0 g, 11.3 mmol) was added to a mixture of 2.0 g (2.8 mmol) 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid bisanhydride and 40 mL propionic acid under an N_2 atmosphere; the reaction mixture was stirred and heated at 140 °C for 10 h. After being cooled to room temperature, the solvent was removed by rotary evaporation, and the crude product was purified by silica-gel column chromatography (eluent: petroleum ether–dichloromethane = 1:1 v/v) to yield perylene bisimide product as a red-brown solid (2.38 g, 85%). ^1H NMR (CD_2Cl_2, 400 MHz): 8.95 (s, 4H), 7.56 (t, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 4H), 2.75 (m, 4H), 0.89 (d, $J = 5.2$ Hz, 24H).

1,6,7,12-Tetrakis(4-iodophenoxy)-N,N′-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (3). Tetrabromoperylenetetracarboxdiimide (2.0 g, 1.95 mmol) was stirred with p-iodophenol (2.57 g, 11.7 mmol) in 1-methyl-2-pyrrilidone (NMP) (100 ml) at 80 °C in a 250-ml flask in the presence of powdered anhydrous K_2CO_3 (0.82 g, 5.9 mmol) under an N_2 atmosphere overnight. Then the reaction mixture was cooled to room temperature and poured into hydrochloric acid (300 ml, 2 N). The precipitated product was filtered under suction, washed three times with water (100 mL), and dried at 75 °C under vacuum. The crude product was purified by column chromography (eluent: petroleum ether/dichloromethane = 1:2 v/v) to give a red solid (2.47 g, 80%). ^1H NMR (CD_2Cl_2, 400 MHz): 8.12 (s, 4H), 7.54 (d, $J = 8.8$ Hz, 8H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 4H), 6.68 (d, $J = 8.8$ Hz, 8H), 2.58 (m, 4H), 1.02 (d, $J = 8.0$ Hz, 24H). Field desorption ionization mass spectrometry (FD-MS): m/z: 1584.8 (100%) $[M]^+$ (calcd. 1584).

1,6,7,12-Tetrakis[4-(trimethylsilylethynyl)phenoxy-N,N′-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (4). Compound **3** (1.0 g, 0.63 mmol) was dissolved in a degassed mixture of triethylamine (20 mL) and absolute THF (10 mL) under N_2. $[PdCl_2(PPh_3)_2]$ (90 mg, 5 mol%), CuI (60 mg, 0.315 mmol), and PPh_3 (89 mg, 0.34 mmol) were then added under a flow of N_2. After the flask was sealed with a septum, trimethylsilylethyne (0.45 ml) was injected. The reaction mixture was stirred at room temperature overnight and then poured into an equal volume of dichloromethane and filtered. The solvent was removed, and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3:2 v/v) to afford **4** (0.77 g, 85%). ^1H NMR (CD_2Cl_2, 400 MHz): 8.12 (s, 4H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 8H), 6.83 (d, $J = 8.0$ Hz, 8H), 2.60 (m, 4H), 1.01 (d, $J = 6.8$ Hz, 24H), 0.15 (s, 48H). FD MS: m/z: 1462.5 (100%) $[M]^+$ (calcd. 1464).

1,6,7,12-Tetrakis(4-ethynylphenoxy)-N,N′-(2,6-diisopropylphenyl)perylene-3,4,9,10-tetracarboxdiimide (5). Compound **4** (50 mg, 0.034 mmol) and NH_4F (10.1 mg, 0.27 mmol) were dissolved in THF (5 mL) under N_2. A solution of n-Bu_4NF (1.3 mg, 0.005 mmol) in THF was added by injection. The mixture was stirred at room temperature overnight. Then the solvents were removed in vacuum, and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 1:2 v/v) to give a red solid 5 (35 mg, 87%). ^1H NMR (CD_2Cl_2, 250 MHz): 8.15 (s, 4H), 7.38 (d, $J = 7.5$ Hz, 8 H), 7.25 (t, 2H), 6.87 (d, $J = 7.5$ Hz, 8H), 3.05 (s, 4H), 2.59 (m, 4H), 1.02 (d, $J = 7$ Hz, 24H). FD MS: m/z: 1176 (100%) $[M + H]^+$ (calcd. 1175.0).

Tetrakis(pentafluorophenyl)cyclopentadienone (6). To a 100-mL round-bottom flask charged with $Co_2(CO)_8$ (1.5 g, 4.5 mmol) and decafluoro-tolane

(1.5 g, 4.4 mmol), o-xylene (25 ml) was injected by syringe under N_2 atmosphere. After rigorously degassing by freeze–pump–thaw, the reaction solution was stirred at room temperature overnight and then heated to reflux under N_2 for 48 h. O-xylene was removed under vacuum, and the crude product was dissolved into 200 mL dichloromethane and passed through a 1-cm high neutral Al_2O_3 pad. Recrystallization from dichloromethane gave a red powder (0.87 g, 54%). Mp = 231.5–232 °C. MS (FD): m/z: 744.8 (M^+). ^{19}F NMR (CD_2Cl_2): $\delta = -136.88$ to -136.91 (d), -137.09 to -137.13 (d), -147.50 to -147.59 (t), -149.68 to -149.77 (t), -158.34 to -158.42 (m), -160.01 to -160.08 (m).

Target dendrimer PDI-F. A solution of 108 mg (0.09192 mmol) **5** and 548 mg (0.7354 mmol) **6** in 15 ml *o*-xylene was stirred and refluxed for 7 days under an atmosphere of dry nitrogen. After cooling to room temperature, the solvent was evaporated under reduced pressure. The crude product was purified by flash-column chromatography over silica gel with mixed petroleum ether and dichloromethane (3:2 v/v) as eluent to give 300 mg pure product as red powder. Yield 81%, mp 413 °C. ^{1}H NMR (CD_2Cl_2, 250 MHz): 8.17 (s, 4H), 7.78 (s, 4H), 7.44 (t, $J = 8.0$ Hz, 2H), 7.26–7.23 (d, $J = 7.5$ Hz, 4H), 7.05 (d, $J = 8.5$ Hz, 8H), 6.77 (d, $J = 8.5$ Hz, 8H), 2.66 (m, 4H), 1.03 (d, $J = 7.5$ Hz, 24H). ^{13}C NMR (600 MHz, CD_2Cl_2, 25 °C): $\delta = 163.4$ (C=O), 156.6, 155.8, 146.3, 145.6, 143.2, 141.0, 139.0, 136.3, 135.4, 134.8 134.2, 132.7, 131.2, 130.8, 130.0, 129.2 (d), 127.1, 124.5, 124.0, 122.0, 121.7, 120.2, 113.1, 111.5, 29.6 (CH, isopropyl), 24.1 (CH_3, isopropyl). ^{19}F NMR (CD_2Cl_2, 500 MHz): $\delta = -136.932$ to -138.826 (m), -148.818 to -149.007 (d), -149.628 (s), -150.527 (s), -158.745 to -159.332 (m). MS (MALDI-TOF): m/z: 4039 $[M + H]^+$(calcd. 4038). Elemental analysis calcd. (%) for $C_{192}H_{58}F_{80}N_2O_8$: C, 57.07; H, 1.45; N, 0.69. Found: C, 57.01; H, 1.38; N, 0.73.

CONCLUSIONS

In conclusion, we synthesized and characterized a novel perylenediimide-cored first generation dendrimer PDI-F, which is a promising candidate for application in organic light-emitting diodes, especially for nondoped red-light-emitting diodes. Sixteen pentafluorophenyl rings were grafted as the shell of the bulky nonplanar molecule. Modification to the chemical structure of dendrimers for high fluorescent quantum yield and more saturated red fluorescence is in progress in our laboratory.

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