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Synthesis and properties of novel perylenebisimide-cored dendrimers

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ABSTRACT

A group of perylenebisimide-cored dendrimers with polyphenylene dendrons at four bay positions were synthesized and characterized. The electron-deficient pentafluorophenyl or cyano groups were grafted at the dendrimer surface with the aim to further increase the n-type features of the resulted dendrimers. The electrochemical and optical properties were investigated. All the dendrimers show good solubility and film-forming properties, high EA values of 3.8–3.9 eV, and high fluorescent quantum yields. All these merits indicate that they are potential multifunctional materials for application in optoelectronic devices such as solar cells or organic light-emitting devices.

1. Introduction

Organic semiconductors have attracted tremendous attention for applications in electronic and optoelectronic devices [1–12] such as photovoltaic cells [2–5], light-emitting diodes [6–9], and field-effect transistors [10,11]. However, the n-type (electron-transporting) semiconductors still lag behind p-type (hole-transporting) materials in overall performance. And it is desired to design and synthesize new n-type organic semiconductors with high performance and environmental stability [12]. Correspondingly, flexibly functionalized dendrimers, which combine the advantages of small molecules and polymers, have ascended to be promising materials in this area recently [13]. The well-defined three-dimensional dendritic structures can greatly improve the solubility and film-forming ability and make these materials suitable for solution processing with agreeable optoelectronic properties.

One typical feature of the dendrimer is that the core, dendron and surface group can be flexibly and separately functionalized to generate different functional materials [14]. For example, dendrimers with different surface groups have been shown to be promising sensing applications [15], while dendrimers with certain chromophores can serve as emitters in OLEDs and light-harvesting systems [16,17]. Perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs) is a favorite candidate as dendrimer building block since functional groups can be flexibly introduced to either the terminal imide moiety or the bay positions of perylene ring to construct multifunctional molecules [18–20]. More importantly, PBIs possess compact and electron-deficient cores and have great potential as n-type semiconductors [21–23]. In particular, Müllen's group and Tian's team have developed a series of PBI derivatives including PBI-cored dendrimers for use in organic light-emitting diodes and sensing applications [20,24,25]. In our previous report [26] we have applied these concepts to prepare a PBI-cored first-generation dendrimer with fluorinated shell (**G1-F**) and demonstrated that it can be used as n-type material in optoelectronic devices.

To extend this work, we designed and prepared the second-generation analog of **G1-F** (**G2-F**) and dendrimers with cyano peripheries up to the second-generation (**G1-CN** and **G2-CN)** (structures shown in Scheme 1). The electrochemical and optical properties of these dendrimers were investigated and the potential applications were suggested.

2. Experimental

2.1. Materials and instruments

All the reagents are of analytical grade and used as received from commercial sources without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA spectrometer (400 MHz). Chemical shifts were referenced to TMS. Mass spectra were recorded on a Micromass Q-Tof (Micromass, Wythenshawe, UK)

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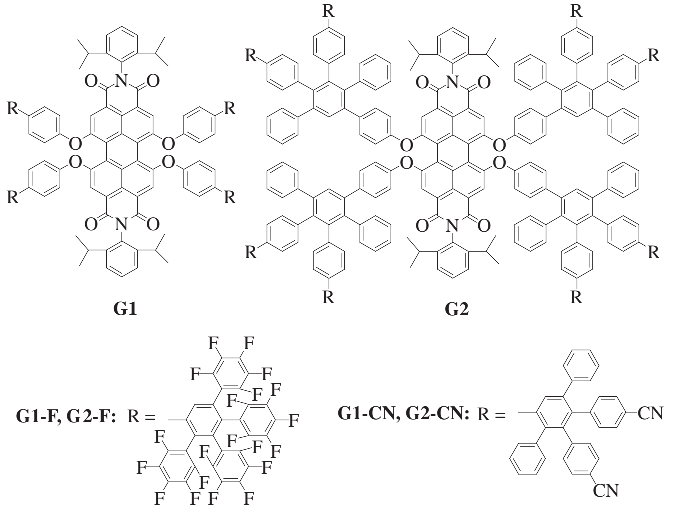


Scheme 1. Chemical structures of the studied dendrimers.

mass spectrometer for ESI–MS and a Micro MX (Micromass) Mass Spectrometer for MALDI–TOF-MS. The fluorescence and absorption spectra were measured on a Perkin–Elmer LS55 fluorescence spectrometer and a Perkin–Elmer Lambda 35 UV–Vis spectraphotometer, respectively. For the solution spectra, dendrimers were dissolved in chloroform (ca. 10^{-5} M) and then put in a quartz cell for measurement. For the thin film spectra, dendrimers were first dissolved in CH_2Cl_2 and then spin-coated onto quartz substrate.

2.2. Electrochemistry

Cyclic voltammetry (CV) measurements were performed using a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode on a computer-controlled BAS 100W electrochemical analyzer at room temperature. The dendrimers were dissolved in dichloromethane solution containing Bu_4NPF_6 (0.1 M) as a supporting electrolyte. The redox potentials were obtained at the scan rate of 100 mV/s. The Ag/AgCl reference electrode was calibrated by ferrocene/ferrocenium (Fc/Fc^+) as the internal standard and all potentials are versus Fc/Fc^+. The HOMO and LUMO energy levels of the studied dendrimers were determined from the onset oxidation (E_{ox}^{onset}) and reduction (E_{red}^{onset}) potential, based on the reference energy level of Fc/Fc^+ (4.8 eV below the vacuum level) [27], according to the following equations:

$$\text{HOMO (eV)} = -e\left(E_{ox}^{onset} + 4.8\ \text{V}\right) \tag{1}$$

$$\text{LUMO (eV)} = -e\left(E_{red}^{onset} + 4.8\ \text{V}\right) \tag{2}$$

2.3. Synthesis

2.3.1. Synthesis of ***G1-core*** and ***G2-core***

The synthesis of these key intermediates **G1-core** and **G2-core** followed the literature methods [28]. They were obtained as red powders.

2.3.1.1. G1-core. ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.13 (*s*, 4H, ArH), 7.54 (*d*, 8H, ArH), 7.39 (*t*, 2H, ArH), 7.24 (*d*, 8H, ArH), 3.54 (s, 4H, ≡CH), 2.59 (*m*, 4H, CH isopropyl), 1.02 (*d*, 24H, CH_3 isopropyl). ESI–MS (*m/z*): calcd. for $C_{80}H_{58}N_2O_8$ 1175.33; found 1176 (100%) $[M + H]^+$.

2.3.1.2. G2-core. ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.13 (s, 4H, ArH), 7.58 (s, 4H, ArH), 7.93 (*t*, $J = 7.8$ Hz, 2H, ArH), 7.32 (*d*, $J = 8.5$ Hz, 4H, ArH), 7.14–6.65 (*m*, 88H, ArH), 3.03 (*s*, 4H, ≡CH), 3.01 (*s*, 4H, ≡CH), 2.68 (*m*, 4H, CH isopropyl), 1.09 (d, 24H, CH_3 isopropyl). MALDI–TOF-MS (*m/z*): calcd. for $C_{208}H_{138}N_2O_8$ 2791.0453; found 2792.2114 (100%) $[M + H]^+$.

2.3.2. Synthesis of tetrakis(pentafluorophenyl)cyclopentadienone (***Cp-F***)

To a 100 mL round-bottom flask charged with $Co_2(Co)_8$ (1.5 g, 4.5 mmol) and decafluoro–tolane **1** (1.5 g, 4.4 mmol), o-xylene (25 ml) was injected by syringe under N_2 atmosphere [29]. 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%). M.p. = 231.5–232 °C. MS (FD) *m/z*: calcd. for $C_{29}F_{20}O$ 744.3; found 744.8 (M^+). ^{19}F-NMR (CD_2Cl_2): δ = −136.88 ∼ −136.91(*d*), −137.09 ∼ −137.13(*d*), −147.50 ∼ −147.59 (*t*), −149.68 ∼ −149.77(*t*), −158.34 ∼ −158.42(*m*), −160.01 ∼ −160.08(*m*).

2.3.3. Synthesis of 4, 4′-Dibromobenzoin (***2***)

A 250 ml round-bottom flask was charged with VB1 (5 g, 20 mmol) dissolved in distilled water (5 ml) and ethanol (100 ml). The mixture was cooled by an ice–salt bath. When the temperature was below zero, a 10% NaOH solution in distilled water was added dropwisely until the pH reached to 9. Then 4-bromobenzaldehyde (20 g, 108 mmol) was added, and the mixture was kept at 65 °C and stirred for 12 h. The solution was cooled and the precipitate was filtered off, washed with water and ethanol. The crude product was a mixture of benzoin and benzil. Crystallization from ethanol gave pure compound **2** (11 g, 55%) as white crystals. M.p.: 92–93 °C (lit. [30]: 94–96.5 °C).

2.3.4. Synthesis of 4, 4′-Dibromobenzil (***3***)

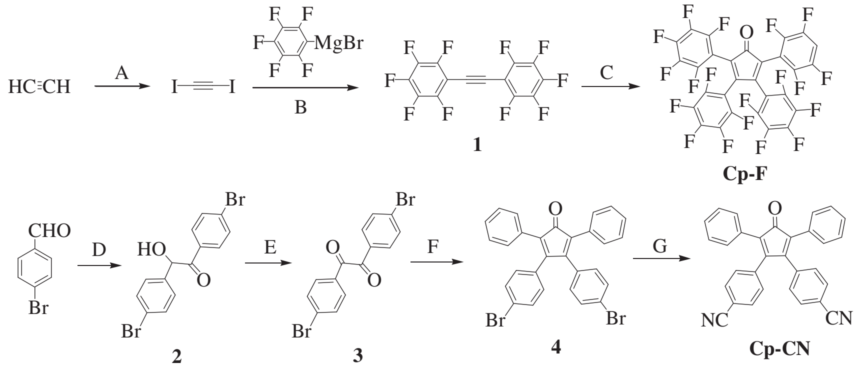
A solution of compound **2** (500 mg, 1.35 mmol), NH_4NO_3 (135 mg, 1.69 mmol), and $Cu(OAc)_2{\bullet}H_2O$ (31.4 mg, 0.17 mmol) in acetic acid (5.5 ml) was stirred and refluxed for 2 h. Upon cooling to room temperature, a precipitate was formed. Filtration followed by washing with water and ethanol gave pure **3** (409 mg, 84.5%) as yellow crystal. M.p.: 230–232 °C. IR (KBr): 3090 (=C–H stretch), 1664 (C=O stretch), 1586 (C=C stretch). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (*d*, $J = 8.4$ Hz, 4H, ArH), 7.67 (*d*, $J = 8.4$ Hz, 4H, ArH). ESI–MS (*m/z*): calcd. for $C_{14}H_8Br_2O_2$ 368.02; found 368 ($[M]^+$).

2.3.5. Synthesis of 3,4-Bis-(4-bromophenyl)-2,5-diphenylcyclopentadienone (***4***)

A 25 ml round-bottom flask was charged with compound **3** (1.2 g, 3.26 mmol), 1,3-diphenylacetone (600 mg, 3.26 mmol), anhydrous KOH (200 mg, 3.59 mmol) and absolute ethyl alcohol (15 ml). The mixture was stirring for 30 min under reflux. Removement of the solvent under reduced pressure gave the crude product, purification of which by column chromatography on silica gel yielded pure compound **4** (1.5 g, 85%) as a dark brown solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.77 (dd, $J = 2.1$, 8.7 Hz, 4H, ArH), 7.1–7.3 (*m*, 10H, ArH), 7.34 (dd, $J = 2.1$, 8.7 Hz, 4H, ArH). ESI–MS (*m/z*): calcd. for $C_{29}H_{18}Br_2O$ 542.26; found 542.0 ($[M]^+$).

2.3.6. Synthesis of 3,4-Bis-(4-cyanophenyl)-2,5-diphenylcyclopentadienone (***Cp-CN***)

A 25 ml round-bottom flask was charged with compound **4** (500 mg, 0.92 mmol), $K_4Fe(CN)_6$ (156 mg, 0.37 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), $P(t\text{-}Bu)_3$ (0.08 ml, 0.03 mmol) and Na_2CO_3



(A) KI, NaOH, NaClO; (B) Mg / Et_2O; (C) $Co_2(CO)_8$; (D) VB1, NaOH, H_2O, EtOH; (E) NH_4NO_3, $Cu(OAc)_2$; (F) KOH, EtOH, 1,3-diphenylacetone, reflux 0.5 h; (G) $K_4Fe(CN)_6$, $Pd(OAc)_2$, P(t-Bu)$_3$, Na_2CO_3, NMP

Scheme 2. Synthetic routes of the important intermediate **Cp-F** and **Cp-CN**.

(39 mg, 0.37 mmol) and NMP (10 ml). The mixture was stirring for 7 h at 140 °C under nitrogen. Removement of the solvent under reduced pressure gave the crude product, purification of which by column chromatography on silica gel yielded pure compound **Cp-CN** (200 mg, 50%) as a dark solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.95 (*d*, J = 8.6 Hz, 4H, ArH), 7.12–7.05 (*m*, 4H, ArH), 7.28–7.20 (*m*, 6H, ArH), 7.45 (*d*, J = 8.6 Hz, 4H, ArH). ESI–MS (*m/z*): calcd. for $C_{31}H_{18}N_2O$ 434.1419; found 434.1423 ($[M]^+$).

2.4. General procedure for synthesis of the target dendrimers

A mixture of **G1-core** (0.13 mmol) or **G2-core** (0.1 mmol) and the corresponding cyclopentadienone (6 equiv. for **G1-core** and 16 equiv. for **G2-core**) in *o*-xylene (15 ml) was stirred at 140 °C for 12 h or 48 h under nitrogen. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel and then recrystallization to afford the target dendrimers. **G1-CN**: yield 63% as a red powder. ^1H NMR (400 MHz, C_6D_6CO) δ (ppm): 8.10 (*s*, 4H, ArH), 7.61 (*s*, 4H, ArH), 7.47–6.82 (*m*, 94H, ArH), 2.78(*m*, 4H, CH isopropyl), 1.14 (d, 24H, CH_3 isopropyl). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 163.1, 155.8, 154.2, 145.6, 144.9, 144.5, 141.2, 140.2, 139.6, 139.1, 138.6, 137.2, 132.9, 132.3, 132.0, 131.5, 131.3, 130.9, 130.5, 129.8, 129.6, 128.6, 128.2, 127.6, 127.2, 126.6, 124.0, 123.1, 120.8, 119.5, 118.6, 110.3, 110.0, 29.2, 24.1. MALDI–TOF-MS: (*m/z*): calcd. for $C_{200}H_{130}N_{10}O_8$ 2799.0073; found 2799.0181 ($[M]^+$).

2.4.1. ***G2-F****: yield 55% as a red powder*

^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.05 (s, 4H, ArH), 7.54–6.85 (*m*, 106H, ArH), 2.6 (*m*, 4H, CH isopropyl), 1.03 (*d*, 24H, CH_3 isopropyl). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 163.1, 155.8, 154.0, 145.6, 145.2, 142.7, 141.3, 141.1, 140.7, 140.4, 140.2, 139.3, 138.8, 138.3, 137.9, 137.7, 136.2, 135.8, 135.5, 135.4, 134.8, 132.9, 131.9, 131.5, 130.6, 129.9, 129.7, 128.6, 128.3, 127.7, 127.2, 126.9, 126.6, 126.0, 124.0, 123.0, 120.7, 120.3, 119.3, 112.4, 111.3, 29.1, 24.0. MALDI–TOF-MS: (*m/z*): calcd. for $C_{432}H_{138}F_{160}N_2O_8$ 8523.4712; found 8524.5791($[M + H]^+$).

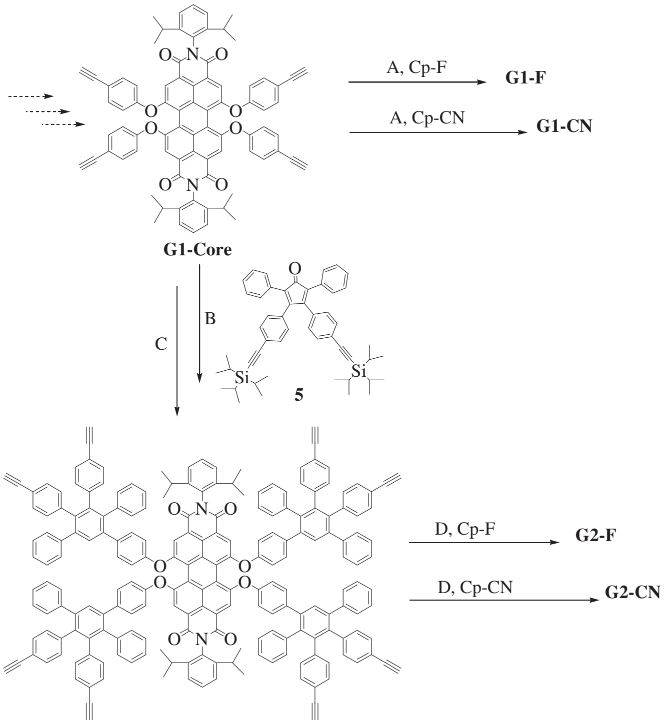
2.4.2. ***G2-CN****: yield 70% as a red powder*

^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): 8.04 (*s*, 4H, ArH), 7.42–6.42 (*m*, 250H, ArH), 2.6(*m*, 4H, CH isopropyl), 1.02 (*d*, 24H, CH_3 isopropyl). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 163.1, 155.8, 153.8, 145.6, 145.0, 144.5, 144.3, 141.6, 141.5, 141.0, 140.9, 140.3, 140.0, 139.7, 139.6, 139.3, 139.1, 138.8, 138.6, 138.3, 138.0, 137.8, 137.4, 137.0, 132.9, 132.0, 131.6, 131.3, 131.2, 130.8, 130.6, 130.0, 129.7, 129.6, 128.9, 128.6, 128.4, 128.2, 128.1, 127.9, 127.7, 127.3, 127.1, 126.3, 126.0, 125.9, 125.8, 125.6, 124.0, 123.0, 120.7, 120.6, 120.3, 119.3, 110.2, 109.9, 29.1, 24.1. MALDI–TOF-MS: (*m/z*): calcd. for $C_{448}H_{282}N_{18}O_8$ 6045.1485; found 6047.3633($[M + H]^+$).

3. Results and discussion

3.1. Design, synthesis and characterization

PBI was selected as the dendrimer core because of its outstanding photophysical and electronic properties with relatively high fluorescent quantum efficiency and high electron affinity and the corresponding n-type characteristics, whose derivatives have



(A) o-xylene, 20 h, reflux; (B) o-xylene, 12 h, reflux; (C) THF, n-Bu_4NF, 30 min., rt.; (D) o-xylene, 48 h, reflux.

Scheme 3. Synthetic routes of the dendrimers.

Table 1
The photophysical and electrochemical data of the studied dendrimers.

Dendrimer	λ_{abs} (nm)[a]			λ_{em} (nm)[b]	Φ_f[c]	E_{red}^{onset}[d] (V)	E_{ox}^{onset}[d] (V)	HOMO (eV)	LUMO (eV)
G1-F	441	525	564	595	0.95	−0.9	–	−5.96[e]	−3.9
G2-F	453	537	579	608	0.93	−1.0	–	−5.85[e]	−3.8
G1-CN	452	536	578	606	0.75	−0.97	0.88	−5.68	−3.83
G2-CN	452	537	579	606	0.62	−1.0	0.84	−5.64	−3.8

[a] Measurements were performed in chloroform solvents (ca. 10^{-5} M).

[b] Measurements were performed in chloroform solvents (ca. 10^{-5} M, excited at 540 nm).

[c] The fluorescence quantum yield (Φ_f) was measured in chloroform solution relative to 1,6,7,12-tetraphenoxy-N,N′-bis(2,6-diisopropyl-phenyl)perylene-3,4,9,10-bis(dicarboximide) in chloroform (96%) (Excited at 540 nm).

[d] All potential values are versus Fc/Fc$^+$.

[e] Calculated from the optical band gap.

been widely used for electronic and optoelectronics devices [18–26]. The polyphenylene dendrons were selected to build up the dendrimers due to their famous merits of non-planar steric conformation and excellent thermal stability [31]. The pentafluorophenyl or cyano groups were grafted to the dendrimer surface to further increase the n-type feature of the target dendrimers based on their strong electron withdrawing nature. The dendrimers designed in this way can be expected to have high luminescent efficiency, good thermal and morphological stability, high electron affinity and good film-formation ability by solution processing methods, so that they can be potentially used as multifunctional materials in optoelectronic devices.

The traditional divergent approach was employed to synthesize the second-generation dendrimers in this study. The polyphenylene dendrons of the studied dendrimers were constructed by Diels–Alder cycloaddition of tetraphenyl-cyclopentedieneone to the terminal ethynyl groups at the periphery of the PBI core. The important building blocks of **Cp-F** and **Cp-CN** for the synthesis of the target dendrimers were prepared according to the methods as described in Scheme 2. **Cp-CN** was synthesized by a four-step reaction procedure. The first intermediate compound **2** was prepared by benzoin condensation with 4-bromobenzaldehyde as the starting material in the presence of vitamin B1 and NaOH in ethanol. It was found that when the pH was higher than 9 or the temperature was higher than 65 °C, the product yield was decreased or even no product was observed. This indicates that the pH and temperature are two key factors for the reaction as they control the formation of the yield of thiamine that is essential for the catalysis of the benzoin condensation [32]. Interestingly, two new spots were observed on TLC analysis corresponding to compound **2** and **3**, implying that compound **2** was partly oxidized during the reaction. Without further purification, the mixture of **2** and **3** was directly oxidized with NH_4NO_3 and $Cu(OAc)_2$ to give compound **3** completely, which condensed with 1,3-diphenylacetone to afford the compound **4** with a high yield. Cyanization of compound **4** by $K_4Fe(CN)_6$ in the presence of $Pd(OAc)_2$, $P(t\text{-}Bu)_3$ and Na_2CO_3 in NMP generated the important intermediate **Cp-CN** as a black solid. Instead of CuCN or KCN, we took $K_4Fe(CN)_6$ as the cyanization reagent mainly for the sake of safety.

The target dendrimer**s** were synthesized through the procedure described in Scheme 3. All the dendrimers were prepared in the divergent way from the perylenebisimide-containing core, the so-called first-generation core (**G1-Core**). The first-generation dendrimers, **G1-F** and **G1-CN**, were obtained in high yields by Diels–Alder cycloaddition of the corresponding **Cp-F** and **Cp-CN** to **G1-Core**. Cycloaddition with intermediate **5** followed by deprotection transformed **G1-Core** to the second-generation core **G2-Core**, the cycloaddition of which with the **Cp-F** and **Cp-CN** once again gave rise to the second-generation dendrimers **G2-F** and **G2-CN**. Since the reactive sites in **G2-Core** are two-fold higher than in **G1-Core**, a higher reaction temperature and much longer reaction time were necessary to guarantee the complete transformation of the ethynyl groups and thus a monodispersity of the target dendrimers. All these dendrimers are highly soluble in common solvents such as dichloromethane, chloroform, or toluene and were purified conveniently by column chromatograph and recrystallization to an excellent purity. Characterization by MALDI-TOF mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy unambiguously confirmed the chemical structures of these dendrimers.

3.2. Electrochemical properties

In order to determine the redox properties of these dendrimers, cyclic voltammtry (CV) was performed in dichloromethane solutions. From these data, HOMO and LUMO energy levels and the band gaps were estimated and are summarized in Table 1. The cyclic voltammograms of these materials are shown in Fig. 1.

In the reductive potential region, two reversible waves are observed for all dendrimers, indicating stepwise single-electron reduction and radical anion and dianion generation on the perylenebisimide core [33]. For the first-generation dendrimer **G1-F** and **G1-CN**, both the first and second reduction waves are at less negative potentials than those

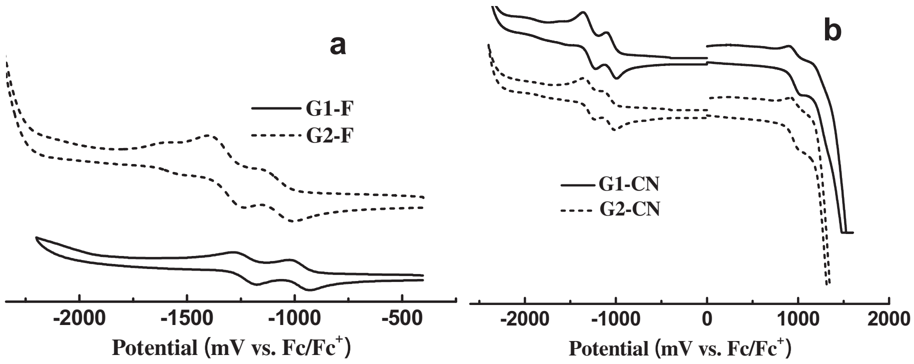


Fig. 1. Cyclic voltammograms of studied dendrimers.

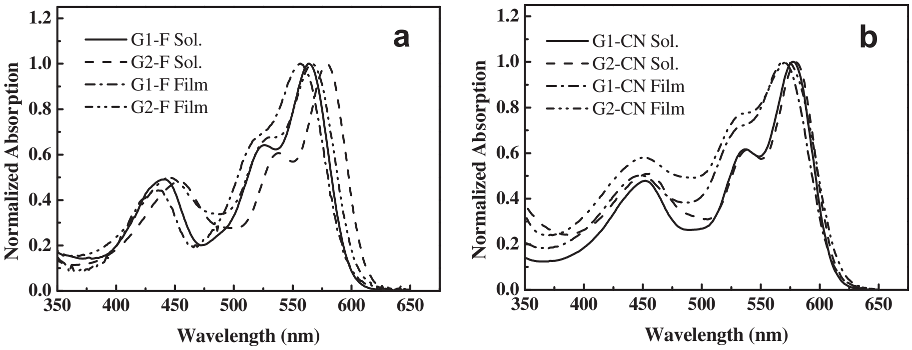


Fig. 2. UV–Vis absorption spectra of the dendrimers in chloroform and thin films.

for their corresponding second-generation analogs, indicating that the first-generation dendrimers capture electrons more easily. This is due to the "dendrimer effect", i.e., the thicker the dendron shielding surrounding the PBI core, the more difficult for the internal PBI core to accept electrons from outside. In the positive potential region, no oxidation was observed for the fluorinated dendrimers, whereas one reversible wave was observed for **G1-CN** and **G2-CN**. The absence of any oxidation in fluorinated dendrimers should result from the combined effects of the inherent n-type nature of the PBI core and the additional strong electron withdrawing properties of the peripheral pentafluorophenyl moieties. Similarly with increasing size and generation of the polyphenylene dendrons, the oxidation wave of the **G2-CN** dendrimer shifted to slightly higher potential than **G1-CN**. The electron affinity (EA, corresponding to LUMO energy level) and ionization potential (IP, corresponding to HOMO level) were determined from the onset potential of the first reduction (E_{red}^{onset}) wave and the first oxidation (E_{ox}^{onset}) wave, respectively, by using an Fc/Fc$^+$ energy level of −4.8 eV vs vacuum [27]. The electron affinity was in the range of 3.8–3.9 eV for these four dendrimers. The IPs for **G1-CN** and **G2-CN** are 5.68 and 5.64 eV, respectively. Since no oxidation process was detected for **G1-F** and **G2-F**, their IPs were estimated as ca. 5.96 and 5.85 eV, respectively, from the optical band gap and EA data according to the equation of $IP = EA + E_g$.

The high electron affinities of 3.8–3.9 eV for these PBI-cored dendrimers with strong electron withdrawing peripheral groups imply that these dendrimers are promising materials to act as electron acceptors for solar cells or other optoelectronic devices, in which a high electron affinity of the n-type material is one essential parameter to influence the device performance.

3.3. Optical properties

Due to the non-planar molecular conformation aroused from the bulky polyphenylene dendrons, these PBI-cored dendrimers have good solubility in common organic solvents and form high-quality films when spin-coated from solutions onto quartz. The optical properties of **G1-F**, **G2-F**, **G1-CN** and **G2-CN** were therefore easily investigated in both solutions and films. Their absorption spectra in chloroform solutions and films are shown in Fig. 2. Two main bands, in the ranges 480–600 nm and 400–460 nm, can be observed from the spectra. Between 480 and 600 nm the absorption can be assigned to the S_0–S_1 electronic transition (along the long PBI axis). The second absorption band between 400 and 460 nm is ascribed to the S_0–S_2 electronic transition (along the short PBI axis) [28]. In contrast to the frequently observed bathochromic effect due to intermolecular interaction in solid samples, the absorption spectra of thin films of the present dendrimers were blue-shifted by about 10 nm relative to those in solutions. The hypsochromic effect in the absorption spectra implies the tiny intermolecular interaction in the solid films of these dendrimers, which should benefit from the non-planar molecular conformation of these bulky dendrimers. The broad light absorption in visible light range together with high EA value suggests that these dendrimers are good candidates for use in solar cells.

Fig. 3 illustrates the photoluminescence (PL) spectra of these dendrimers in chloroform solutions and thin films. Under excitation at 540 nm, all these dendrimers emit strong red fluorescence in both solutions and thin films. In solutions, the fluorescence maxima are located at 595, 608, 606 and 606 nm for **G1-F**, **G2-F**, **G1-CN** and **G2-CN**, respectively, while the corresponding maxima for the films are at 594, 614, 630 and 618 nm, respectively. Apparently, the red emission of these dendrimers is emitted from the PBI core. Similar to the hypsochromic effect in the absorption spectra, the relatively small red-shifts observed in PL spectra once again indicate the weak intermolecular interaction of the emissive core which is caused by the perfect site-isolation or dendron dilution effect on the emissive core.

The fluorescence quantum yields of these dendrimers (excited at 540 nm) were measured in chloroform relative to 1,6,7,12-tertraphenoxy-N,N′-bis(2,6-disisopropyl-phenyl)perylene-3,4,9,10-bis(dicarboximide) (96% in chloroform) [34]. All dendrimers

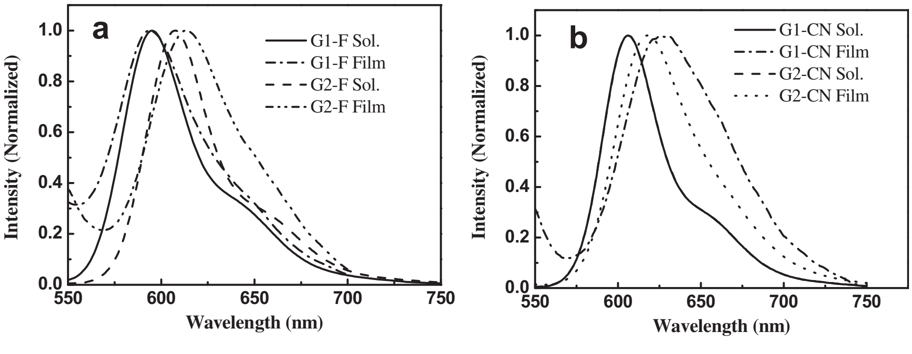


Fig. 3. Fluorescence spectra of dendrimers in chloroform and thin films ($\lambda_{exc} = 540$ nm).

exhibit high quantum yields of 0.95, 0.93, 0.75 and 0.62 for **G1-F**, **G2-F**, **G1-CN** and **G2-CN**, respectively. The high fluorescent quantum yields suggest that these dendrimers can be used as red emitters in organic light-emitting diodes.

4. Conclusion

A group of perylenebisimide-cored dendrimers containing polyphenylene dendrons with pentafluorophenyl or cyano surface groups were synthesized and characterized. All the dendrimers show good solubility and film-forming properties, and are characterized by high electron affinities, wide light absorption covering almost the whole visible light range, and high fluorescent quantum yields. All these merits indicate that they are potential multifunctional materials as light-harvesting electron acceptors in solution-processible solar cells or as red emitters for organic light-emitting diodes, respectively.

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