Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 7658–7669

polymer

www.elsevier.com/locate/polymer

# Dendron-functionalized perylene diimides with carrier-transporting ability for red luminescent materials

Jianfeng Pan[a], Weihong Zhu[a], Shangfeng Li[a], Wenjin Zeng[b], Yong Cao[b], He Tian[a,*]

[a]*Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, China*
[b]*Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China*

Received 22 March 2005; received in revised form 23 May 2005; accepted 28 May 2005
Available online 21 June 2005

**Abstract**

This paper presents a series of dendrimers via a convergent synthetic approach with three generations, which contain perylene diimide cores, Fréchet-type poly(aryl ether) dendrons, and carbazole (CZ) or oxadiazole (OXZ) peripheral functional groups. The higher generation dendrimer has an obvious site-isolation or dilution effect of dendrons, which results in a relatively small red-shift of absorption and emission spectra when it forms a solid thin film for applications. The interactions between peripheral units and perylene diimide core in the dendrimers are also studied by steady-state and time-resolved fluorescence spectra under both direct and indirect excitation. The fluorescence data show that there exist two possible mechanisms, Förster energy transfer (FRET) and photo-induced electron transfer (PET), for dendrimers bearing carbazole units. No enhanced core fluorescence is observed because the energy transfer or light-harvesting potential of peripheral carbazole is counteracted by PET. While for dendrimers bearing oxadiazole units, no PET can take place between OXZ and perylene diimide since both of them are high electron affinity. The FRET and higher light-harvesting ability of oxadiazole without PET interfering result in the distinct enhancement of core emission in higher generation dendrimers. DSC results indicate that the incorporation of Fréchet-type poly(aryl ether) dendrons can improve the amorphous property and increase glass transition temperature ($T_g$). The preliminary EL results with single-layer architectures demonstrate that these dendrimers could be utilized as a promising kind of active red luminescent emitters with carrier-transporting ability. EL emission has the same recombination zone as PL, indicating that the recombination of excitons in fabricated EL devices is not close to cathode or anode vicinity. It is suggested that the site-isolation effect of dendron wedges is attributed to prevent the core luminorphores from approaching electrodes efficiently.

*Keywords:* Dendrimers; Perylene diimides; Red luminescence

## 1. Introduction

To date, since various OLEDs based on small molecules [1,2] and polymers [3–5] have been extensively studied, it becomes more and more interesting to develop novel electroluminescent materials, which can combine the advantages of small molecules and polymers. In this regard, several research groups have recently investigated functionalized light-emitting dendrimers as an alternative candidate [6–8]. The beautiful well-ordered dendritic structures can greatly improve the solubility and amorphous phase of chromophores to uniformly develop high quality film with spin-coating technique, which is a prerequisite for a high-efficiency device.

Two unique properties of functionalized dendrimers for emitters are light-harvesting and site-isolation effect [9–12]. In a dendritic antenna, the peripheral donor units can collect photons, and transfer excitation energy through bond to the core or focal point acceptor chromophores, thus greatly enhancing luminescence efficiencies. For example, a phenyl acetylene dendrimer reported by Moore and co-workers shows an energy transfer from the periphery towards the center through the framework, leading to greatly enhanced fluorescence signal [13,14]. Fréchet et al. also have synthesized a series of poly(aryl ether) dendrimers, in which coumarin 2 acts as a light-harvesting antenna at the periphery and coumarin 343 as a focal chromophore acceptor at the core [15,16]. Furthermore, the site-isolation or dilution effect of dendrons enables the processing and

---

[*] Corresponding author. Tel.: +86 21 64252756; fax: +86 21 64252288.
*E-mail address:* tianhe@ecust.edu.cn (H. Tian).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.05.117

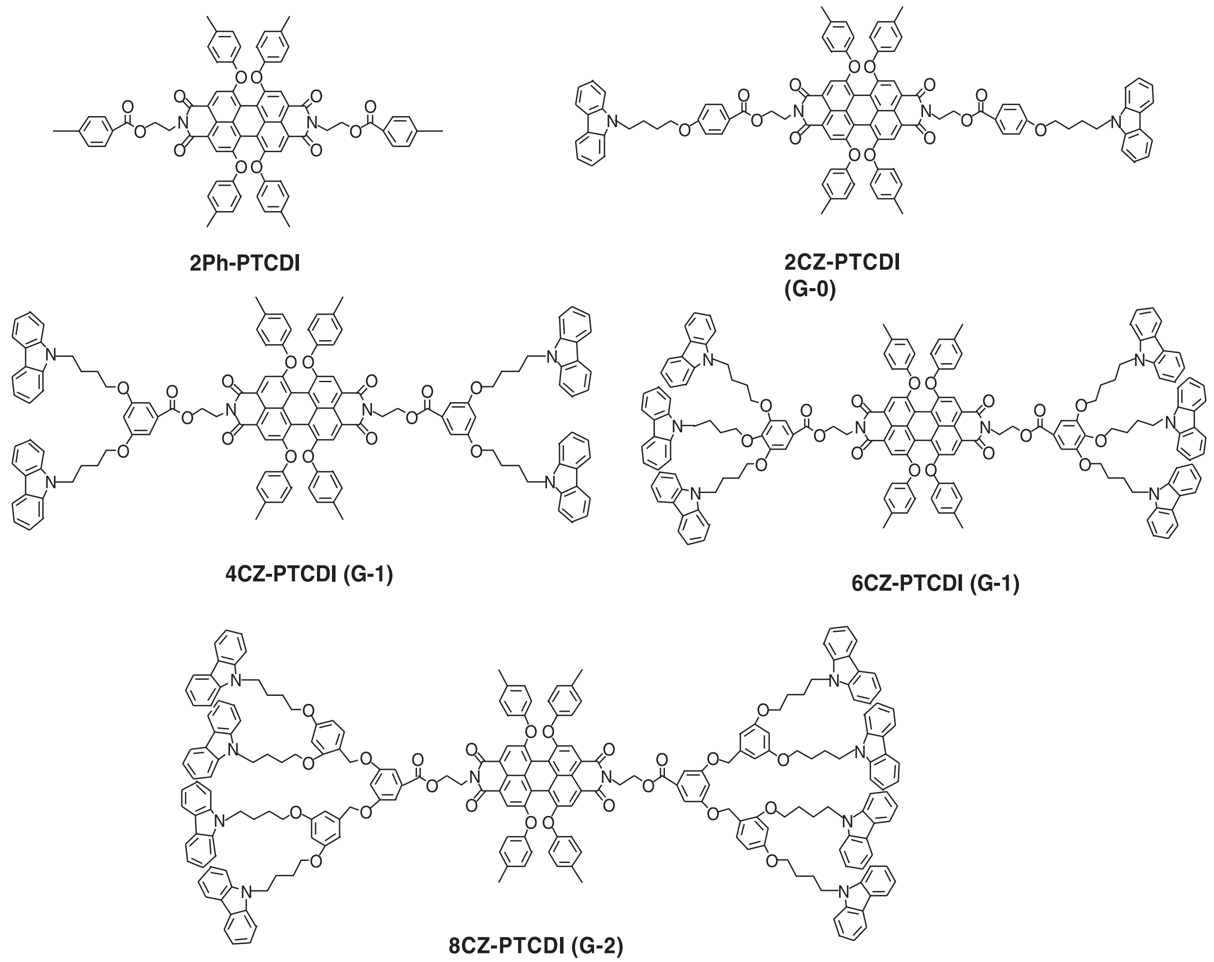
electronic properties to be tuned independently [17,18]. It also can control the intermolecular interactions, and reduce the aggregating extent or possibility of the core unit, thus alleviating the aggregation problem that is known to be detrimental to device efficiency [9,19].

Dye-cored dendrimers can become multi-functional light-emitting materials when proper charge-transporting functionalities are incorporated at the periphery of the dendrons, which can tune unbalanced carrier-transporting properties of luminophores [20,21]. Therefore, dendrimers can provide a new opportunity to precisely place charge-carrier transporting units by growing generations in three-dimensional nanoscale construction. Our group has successfully synthesized a series of naphthalimide dendrimers exhibiting light-harvesting and enhanced core-luminescence properties [22]. To further study the physical chemistry and more specifically the electronic properties of dendron-based chromophores, here we report the opto-electronic properties of a novel series of perylene diimide-based dendrimers as red luminescent materials, bearing carbazole or oxadiazole units on the outer surface of poly(aryl ether) dendritic wedges (Schemes 1 and 2). The absorption, emission spectra, as well as transient fluorescence were also studied to gain insight into the interaction between periphery units and perylene diimide core. It is noted that the pure dendrimers used as host emitter without any matrix is paving a way or allow to fabricate EL devices with printing techniques.

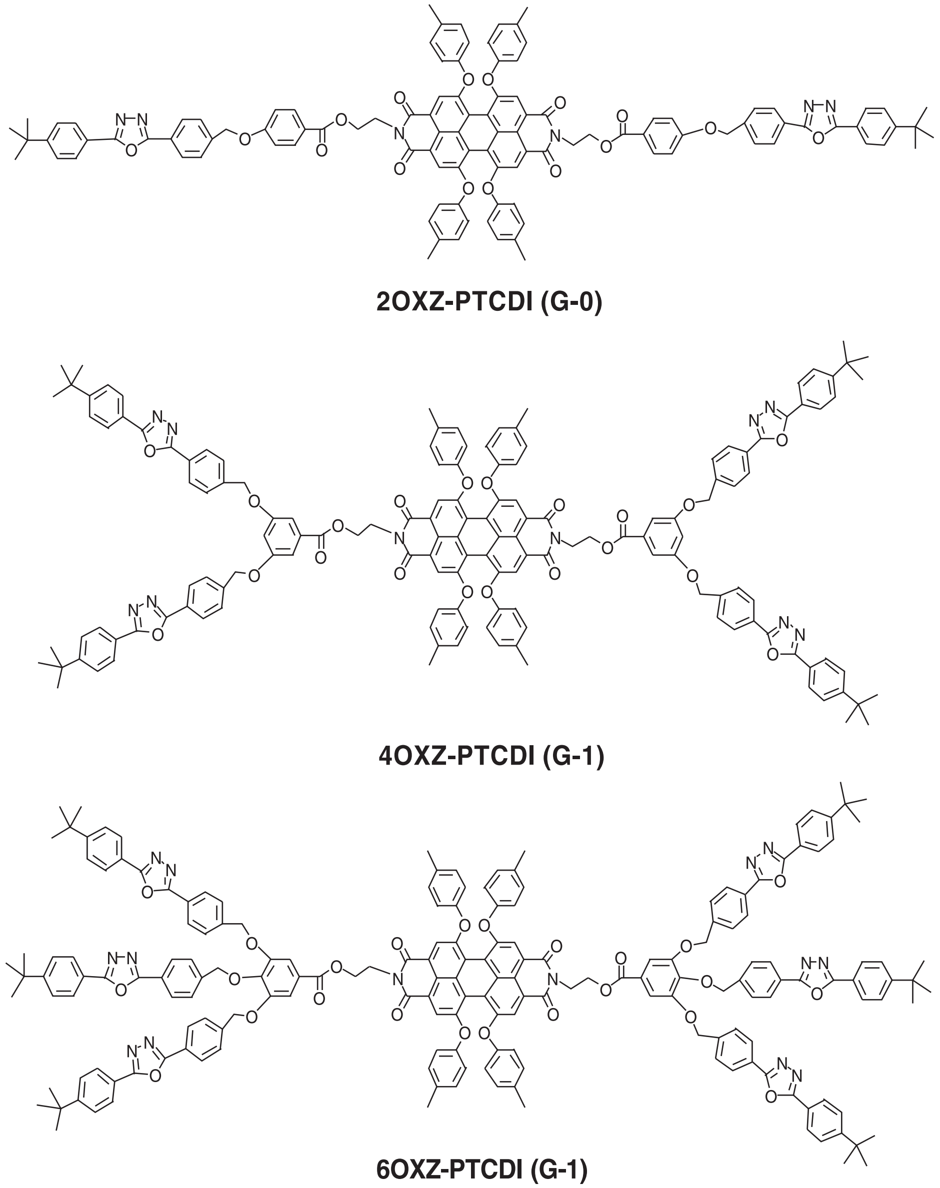
## 2. Results and discussion

### 2.1. Design, synthesis and characterization of luminescent dendrimers

To develop active red luminescent emitters with charge-tunable ability, the dendrimers synthesized here characterize the perylene diimide chromophore at the core of the dendrimer with specific functional groups of carbazole (CZ) or oxadiazole (OXZ) at the periphery constructed by Fréchet-type poly(aryl ether) dendrons (Schemes 1 and 2). We chose perylene diimide as a fluorescent core because of its excellent light/heat stability and high luminescent efficiency, whose derivatives have been widely applied in organic molecular electronics [23–26]. The carbazole (CZ) or oxadiazole (OXZ) units can play a major role in



Scheme 1. Chemical structures of target dendrimers bearing carbazole, and reference compound 2Ph-PTCDI.



**2OXZ-PTCDI (G-0)**

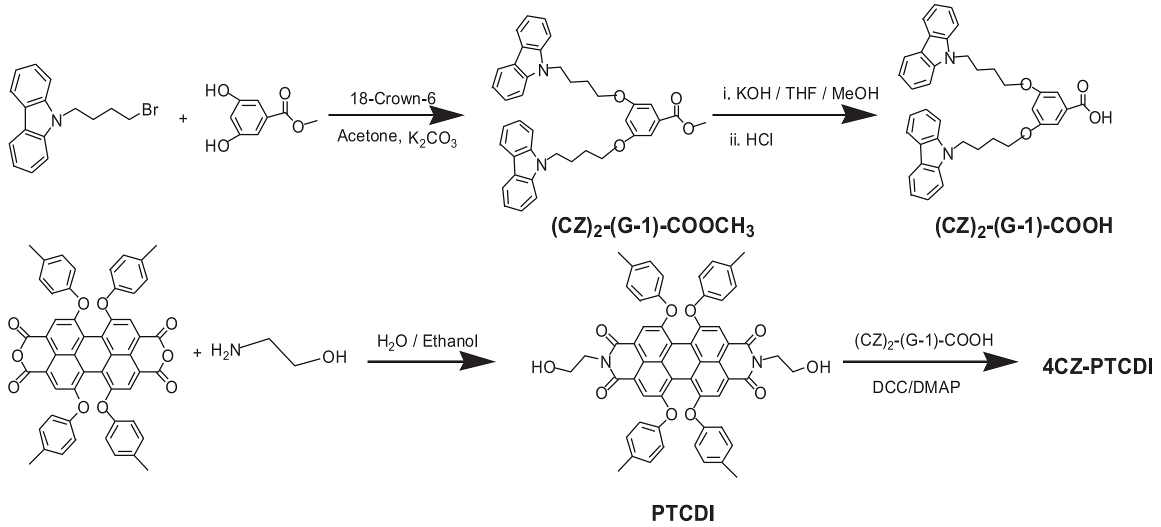
**4OXZ-PTCDI (G-1)**

**6OXZ-PTCDI (G-1)**

Scheme 2. Chemical structures of target dendrimers bearing oxadiazole.

carrier-transporting, and also act as light antennae for the core chromophores. The traditional convergent approach originally reported by Hawker and Fréchet [27,28] was employed to synthesize three generation dendrimers. To illustrate the case, the synthetic route of 4CZ-PTCDI as an example is outlined in Scheme 3. A mixture of *N*-(4-bromobutyl)-9*H*-carbazole, methyl 3,5-dihydroxybenzoate, anhydrous potassium carbonate and 18-crown-6 in anhydrous acetone was refluxed for 60 h with vigorous stirring under argon to obtain $(CZ)_2$–(G-1)–$COOCH_3$ in 94.2% yield, followed by hydrolysis reaction with KOH in 2:1 methanol/THF at reflux to give the first-generation dendron in 95.9% yield. Bromination of benzyl alcohol group of $(CZ)_2$–(G-1)–$CH_2OH$ by treatment with carbon tetrabromide/triphenylphosphine at room temperature in anhydrous $CH_2Cl_2$ proceeded smoothly to afford the corresponding bromide $(CZ)_2$–(G-1)–$CH_2Br$ in 92.1% yield. Repeating the above Williamson ether reaction and hydrolysis reaction in the same conditions to give the second-generation dendron $(CZ)_4$–(G-2)–COOH. Finally, with the assistant dehydration of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP), the esterification of the core intermediate with the corresponding different generation dendrons was easy achieved in anhydrous $CH_2Cl_2$ at room temperature to obtain the final dendrimers 4CZ-PTCDI. The product was purified by column chromatography on silica gel. Similarly, we prepared other target dendrimers. The detailed synthesis and structure characterization will be described elsewhere.

The dendrons and dendrimers were characterized by standard spectroscopic techniques including $^1H$ NMR, $^{13}C$ NMR, and MS (ESI or MALDI-TOF). MALDI-TOF mass



Scheme 3. Synthetic route of first-generation dendrimer 4CZ-PTCDI.

spectroscopy is a very powerful tool to identify such kind of macromolecular dendrimers. For example, in MALDI-TOF mass spectroscopy of 4CZ-PTCDI, the compound shows the corresponding ion peaks of $[M^+]$ centered at *m*/*z* 2058.94, and the peaks centered at *m*/*z* 2081.95 and 2097.93 are ascribed to $[M^+ + Na]$ and $[M^+ + K]$, respectively. It is analogous to 4OXZ-PTCDI, in whose MALDI-TOF mass spectroscopy $[M^+]$ appears at *m*/*z* 2336.96, the peaks of $[M^+ + Na]$ and $[M^+ + K]$ appear at *m*/*z* 2357.93 and 2373.91, respectively.

## 2.2. Absorption spectra

The absorption and emission spectral data of perylene-cored dendrimers in THF and solid film are summarized in Table 1. The series of dendrimers show very similar absorption characteristics both in solution and in solid film. In THF, the absorption peaks at 330 and 345 nm are attributed to the transition absorption of carbazole unit, the absorption peak around at 285 nm is attributed to oxadiazole unit, and the latter three peaks to the characteristic absorption of perylene diimide core. With the generation growth, the absorbance of carbazole units is proportional to the generations within experimental error (Fig. 1). Notably, there is no spectral shift of the absorption band of the peripheral group of carbazole and oxadiazole units with increasing generation (Table 1). The absorption intensity of perylene diimide core in THF does not distinctly change with increasing generation but does exhibit small bathochromic shift, which is attributed to the micro-environment polarity of larger dendritic wedges. Moreover, with respect to the reference compounds of 2Ph-PTCDI and carbazole or oxadiazole, the absorption spectra of all perylene diimide-cored dendrimers are well matched by the sum of the spectra of relative constituent chromophores. In all cases, dendron functionalized backbone does not appear to significantly perturb the electronic transition in the ground state. This provides a window to selectively excite the dendron and the core to study the photoinduced energy-transfer and electron-transfer.

## 2.3. Luminescent properties and light-harvesting

All dendrimers show characteristic luminescence of the core perylene diimide with the peak at around 600 nm (Table 1). Compared with their fluorescence in THF, the fluorescence of dendrimers in solid state is red-shifted, and the red-shifts of 2CZ-PTCDI, 4CZ-PTCDI, and 8CZ-PTCDI are 72, 60, and 51 nm, respectively (Fig. 2). The results indicate that the higher generation dendrimer has a relatively smaller Stokes shift than lower generation one, indicative of a site-isolation or dendron dilution effect to a certain extent, which reduces the aggregating extent or possibility of the core. However, attachment of such

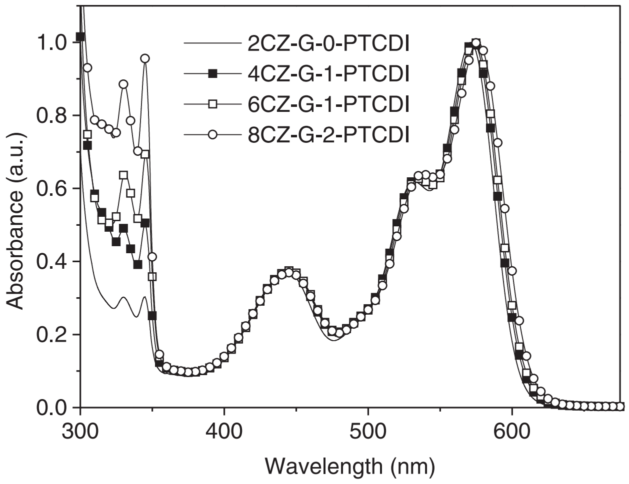


Fig. 1. Normalized absorption spectra of 2CZ-PTCDI, 4CZ-PTCDI, 6CZ-PTCDI and 8CZ-PTCDI in THF ($2.0 \times 10^{-5}$ M).

Table 1
Absorption and fluorescence emission data in THF and thin film for dendrimers

| Dendrimers | In THF | | | | | | In thin film | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{\max}^{\text{abs}}$ (nm, log $\varepsilon$) | | | $\lambda_{\max}^{\text{em}}$ (nm) | | $\eta^{a}$ (%) | $\lambda_{\max}^{\text{abs}}$ (nm) | | | $\lambda_{\max}^{\text{em}}$ $^{b}$ (nm) |
| 2CZ-PTCDI | 330(3.87) | 345(3.87) | | 350 | 365 | 78 | 332 | 346 | | |
| | 444(4.26) | 532(4.48) | 571(4.69) | 601 | | | 456 | 549 | 596 | 673 |
| 4CZ-PTCDI | 330(3.76) | 345(3.77) | | 350 | 365 | 87 | 332 | 346 | | |
| | 445(4.24) | 534(4.47) | 573(4.67) | 601 | | | 457 | 549 | 596 | 661 |
| 6CZ-PTCDI | 330(3.67) | 345(3.70) | | 350 | 366 | 91 | 334 | 347 | | |
| | 445(4.21) | 535(4.44) | 574(4.64) | 602 | | | 460 | 550 | 598 | 671 |
| 8CZ-PTCDI | 330(3.61) | 345(3.64) | | 350 | 366 | 83 | 334 | 349 | | |
| | 445(4.13) | 538(4.37) | 576(4.56) | 602 | | | 461 | 556 | 601 | 653 |
| 2OXZ-PTCDI | 284(4.98) | | | 349 | | 75 | 313 | | | |
| | 444(4.12) | 530(4.31) | 571(4.49) | 602 | | | 456 | 559 | 607 | 668 |
| 4OXZ-PTCDI | 289(5.00) | | | 350 | | 74 | 307 | | | |
| | 446(3.96) | 534(4.15) | 574(4.34) | 605 | | | 454 | 554 | 602 | 655 |
| 6OXZ-PTCDI | 283(5.20) | | | 352 | | 51 | 315 | | | |
| | 446(4.19) | 536(4.38) | 577(4.57) | 606 | | | 458 | 559 | 609 | 672 |

[a] Peripheral donor emission quenching efficiency ($\eta$) was calculated by comparing the integration of donor emission between the simple mixture of $(CZ)_m$–(G-$n$)–$COOCH_3$/or $(OXZ)_m$–(G-$n$)–$COOCH_3$ and 2Ph-PTCDI and the target dendrimer excited at corresponding donor absorption peak.

[b] Excited at 460 nm.

dendrons to the imide moiety of a perylene diimide cannot completely shield the chromophore core.

Dendrimers have an ideal architecture to study the interaction between chromophores [29]. Because there is an overlap between the emission spectra of carbazole or oxadiazole and the absorption of the reference compound of 2Ph-PTCDI, a singlet–singlet Förster energy transfer can take place in these dendrimer systems [30–32], which can be clearly demonstrated in excitation spectra (Figs. 3 and 4). It indicates that the peripheral carbazole and oxadiazole units in such dendrimers based on perylene diimide system can exhibit light-harvesting potential. Thus it is possible to obtain a strong intense emission from the core when excited via sensitization from a large light-harvesting antenna. As mentioned above, we can independently address functionalized dendron units (oxadiazole or carbazole) and core perylene diimide by changing the excitation wavelength when considering the following facts: (1) the absorption spectra of relative units do not overlap; (2) the dendron-functionalized backbone does not significantly perturb the electronic transition in the ground state. When excited at the maximum absorption of peripheral dendron unit of

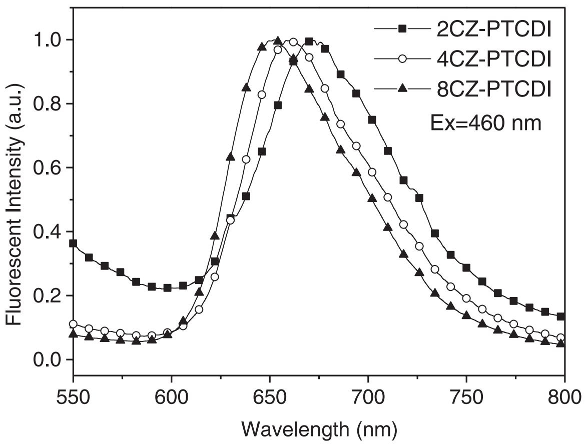


Fig. 2. Normalized fluorescence spectra of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI in solid film excited at 460 nm.

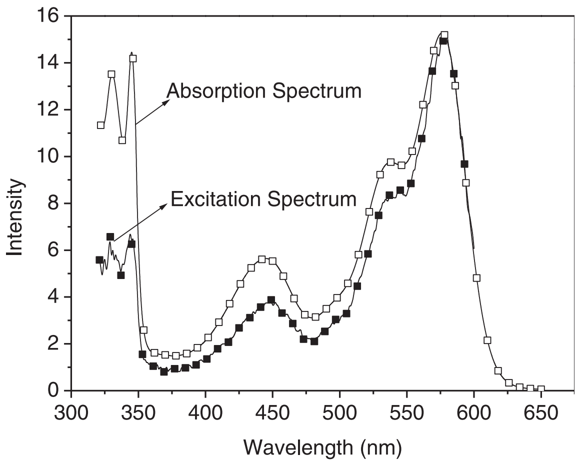


Fig. 3. Absorption and corrected excitation spectra of 8CZ-PTCDI in THF monitored at the core perylene diimide emission wavelength (605 nm). The excitation spectra were normalized at the core absorption.

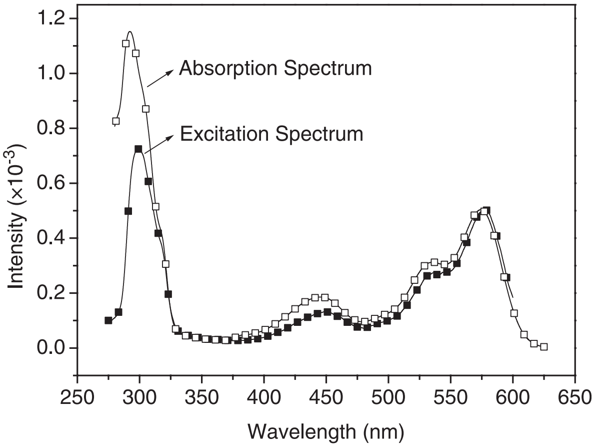


Fig. 4. Absorption and corrected excitation spectra of 4OXZ-PTCDI in THF monitored at the core perylene diimide emission wavelength (605 nm). The excitation spectra were normalized at the core absorption.

oxadiazole units (285 nm) (Fig. 5), the sensitized emission intensities of the core perylene diimide for 6OXZ-PTCDI, 4OXZ-PTCDI and 2OXZ-PTCDI are 6:3.5:1, respectively. Clearly, the more number of the grafted oxadiazole unit in the dendron, the higher light-harvesting capability. Moreover, the emission intensity of the core for 6OXZ-PTCDI excited at 285 nm is about 20% higher than that of the direct core excitation (570 nm). That is, the intensity of the harvested core emission for the dendrimers bearing oxadiazole units can be stronger than that of the core emission under the direct core excitation due to strong light-harvesting potential and high efficient energy transfer [33].

When compared with the simple mixture of reference compounds containing carbazole and perylene diimide units in THF excited at the absorption peak of carbazole unit (330 nm), only the core emission of 2CZ-PTCDI was increased and the other three decreased (Fig. 6). That is, 2CZ-PTCDI has a 1.6-fold increase while 4CZ-PTCDI, 6CZ-PTCDI and 8CZ-PTCDI have 3.0-fold, 3.7-fold and 2.1-fold decrease, respectively.

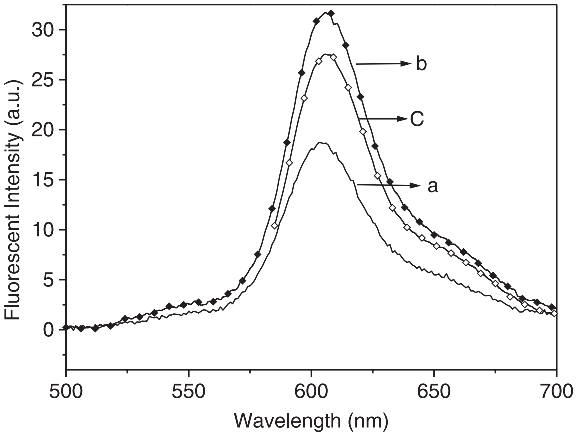


Fig. 5. Fluorescence spectra in THF ($2.0\times10^{-6}$ M): (a) 4OXZ-PTCDI excited at 285 nm, (b) 6OXZ-PTCDI excited at 285 nm and (c) 6OXZ-PTCDI excited at 570 nm.

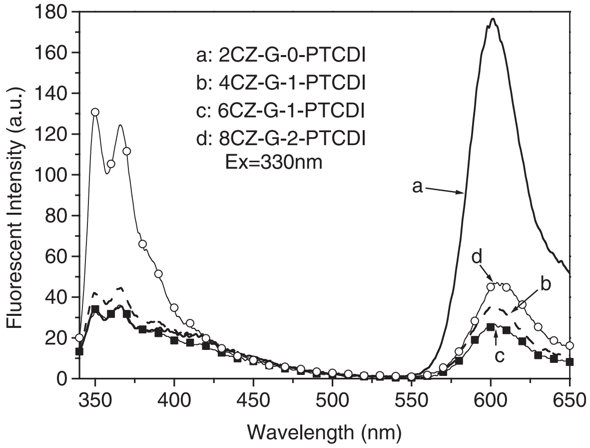


Fig. 6. Fluorescence spectra of 2CZ-PTCDI, 4CZ-PTCDI, 6CZ-PTCDI, and 8CZ-PTCDI in THF ($2.0\times10^{-6}$ M) excited at the absorption peak of carbazole unit (330 nm).

Hence, as expected, the oxadiazole units in the dendrimers bearing oxadiazole exhibit significant light-harvest for the luminescence of perylene diimide cores. However, an apparent paradox arises for the carbazole units in the dendrimers bearing carbazoles, where the data suggest that the fluorescence intensity of perylene diimide core in higher generation dendrimers (G-1, G-2) is apparently lower than that of the G-0 dendrimer. Here the energy transfer or light-harvesting potential of peripheral carbazole might be covered up or counteracted by other possible quenching channels, which can be further supported by a comparison of the core emission intensity under direct excitation (Figs. 7 and 8).

## *2.4. Photo-induced electron transfer (PET)*

Under the direct excitation of the core, the Förster energy transfer between the periphery donors and the core acceptor can be neglected since the direct excitation wavelength

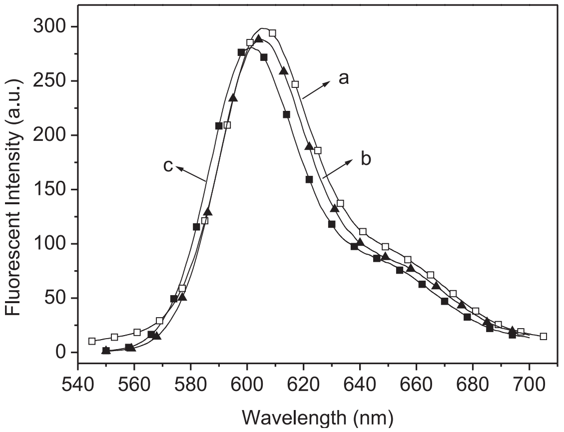


Fig. 7. Fluorescence spectra in THF ($1.2\times10^{-6}$ M): (a) 2OXZ-PTCDI, (b) 4OXZ-PTCDI and (c) 2Ph-PTCDI under direct excitation of core perylene diimide (540 nm). Their absorbance of perylene diimides units is kept nearly same.

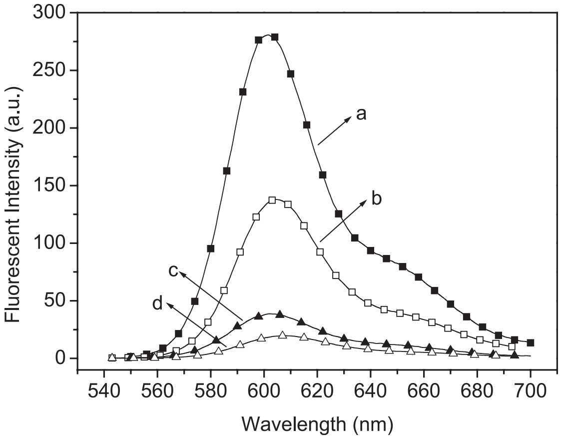


Fig. 8. Fluorescence spectra in THF ($1.2\times10^{-6}$ M): (a) 2Ph-PTCDI, (b) 2CZ-PTCDI, (c) 4CZ-PTCDI and (d) 8CZ-PTCDI under direct excitation of core perylene diimide (540 nm). The absorbance of perylene diimides units is kept nearly same.

(540 nm) is only at the perylene diimides absorption region. If there is no other quenching pathway, the emission intensity of the core perylene diimide should be equal under the direct excitation when keeping the same optical density of the core. As expected shown in Fig. 7, the intensities of the core emission for dendrimers bearing oxadiazole units under direct excitation are almost same within experimental deviation. However, under direct excitation, the intensities of the core emission for dendrimers bearing carbazole units are decreased sharply with increasing the dendron generation (Fig. 8). If comparing with the reference compounds 2Ph-PTCDI (arbitrarily defined to unit), the core emission intensities of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI are 0.48, 0.14 and 0.07, respectively.

Clearly, in contrast to oxadiazole units, the peripherial carbazole units can result in additional quench, and have great effect on the core emission for dendrimers bearing carbazole units under direct excitation. To keep in mind that perylene diimide derivatives have a high electron affinity (3.9 eV of LUMO orbital energy of core perylene diimide, see below), the occurrence of photo-induced electron transfer (PET) is very reasonable when incorporated low oxidation potential units, such as carbazole, to perylene diimide core [34,35]. It is expected that PET from the carbazole units to the excited perylene core quenches the core fluorescence under the direct excitation (Fig. 8). Thus, when excited at the maximum absorption of peripheral carbazole (indirect excitation) for the dendrimers bearing carbazole units, the core luminance of perylene diimide unit is mostly resulted from the competitive action of Förster energy transfer (FRET) and PET between the core perylene diimide and the peripheral carbazole units (Fig. 9). In this case, PET plays major role in the fluorescence quench of perylene diimide in higher generation dendrimers than in the lower generations. Here, since the energy transfer or light-harvesting potential of peripheral carbazole is covered up or counteracted by PET, no enhanced core fluorescence is observed in the system of dendrimers bearing carbazole units.

Another story is for dendrimers bearing oxadiazole units. As discussed above, we can definitely rule out the quenching possibility of PET between the core and peripherial oxadiazole units since the intensities of the core emission are almost same under the direct excitation when keeping the same optical density of the core. The fact that no PET can take place between oxadiazole units and perylene diimide is reasonable since both of them are units with high electron affinity. Hence, under the same indirect excitation (Fig. 10), the energy transfer or light-harvesting of oxadiazole units will not be counteracted by PET, which can clarify the fact that the intensity of the harvested emission for the dendrimers bearing oxadiazole units can be stronger than that of the core emission under the direct core excitation. Additionally, the extinction coefficient (Table 1) and emission intensity of oxadiazole is higher than that of carbazole (2.7 times higher than that of carbazole by comparing the integration of emission between $(CZ)_2$–(G-1)–$COOCH_3$ and $(OXZ)_2$–(G-1)–$COOCH_3$ at the same condition), indicating that the light-harvesting ability of oxadiazole is higher than that of carbazole. Therefore, it is energy transfer/light-harvesting, and higher extinction coefficient and emission intensity of oxadiazole unit that result in the distinct enhancement of the core emission in higher generations for the dendrimers bearing oxadiazole units (Fig. 5).

To estimate the extent of energy transfer in these dendrimers [36,37], we compared the absorption and excitation spectra of dendrimers by monitoring the emission of the acceptor of perylene diimide (605 nm). While normalizing for the peaks corresponding to the acceptor, the relative ratio of the intensity areas of the peaks corresponding to the donor was used to estimate the energy transfer efficiency. Thus, the energy transfer efficiencies are 51, 63 and 66% for 2OXZ-PTCDI, 4OXZ-PTCDI and 6OXZ-PTCDI, respectively. However, such estimation of energy transfer efficiency is not valid for dendrimers bearing carbazole units since the precondition of the approach is that the acceptor quantum yield has to remain constant upon both direct and sensitized excitation. Significant errors can be introduced to the dendrimers bearing carbazole units, which has another quenching channel of PET between donor and acceptor.

Photo-induced electron transfer (PET) between the core and peripheral units are further studied by transient fluorescence spectra. As listed in Table 2, the fluorescence lifetimes of the dendrimers bearing carbazole units are strongly dependent on solvent polarity. The quenching resulted from PET should become more pronounced in polar solvents, which can increase the CT rate. Indeed, this is what is seen in Table 2, where the acceptor decay for the dendrimer becomes slower in non-polar solvent ($C_6H_{12}$) than in polar solvent (THF). In contrast to reference compounds exhibiting only a single exponential fluorescent

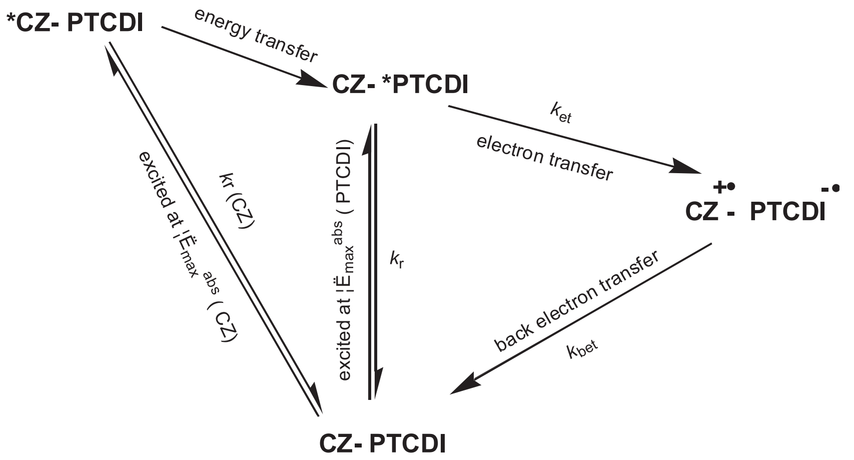


Fig. 9. Schematic diagram for photo-induced energy transfer and electron transfer in dendrimers bearing carbazole units CZ-PTCDI. Due to the high electron affinity of PTCDI and low oxidation potential of carbazole (CZ), the light-harvesting potential of peripheral carbazole is counteracted by PET.

decay, the carbazole units in 4CZ-PTCDI and 8CZ-PTCDI have dual-exponential decay characteristics (Fig. 11). The relatively short-lived fluorescent lifetime component can be assignable to electron communications, that is, photo-induced electron transfer from the excited state of carbazole units to perylene diimide core (Fig. 9). Comparing the shorter lifetime components of the G-1 dendrimer 4CZ-PTCDI and the G-2 dendrimer 8CZ-PTCDI, the fluorescence of perylene diimide core in 4CZ-PTCDI is more severely quenched due to more effective PET from carbazole units to perylene diimide core. Using the calculation method reported on the literature [29] and the data in Table 2, the calculated PET efficiency is about 77.3 and 72.9% for 4CZ-PTCDI and 8CZ-PTCDI in $CH_2Cl_2$, respectively.

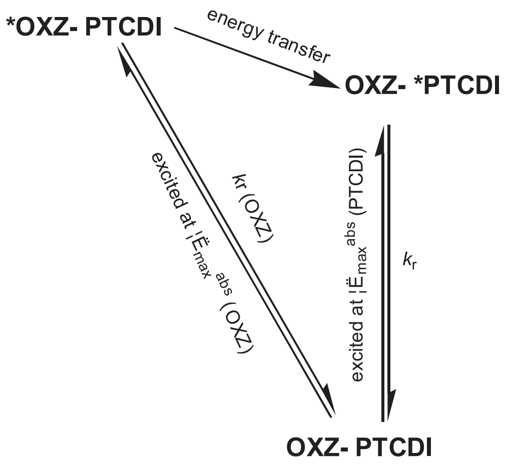


Fig. 10. Schematic diagram for energy transfer in dendrimers bearing oxadiazole units (OXZ-PTCDI). Due to the high electron affinity of oxadiazole (OXZ) and PTCDI, no PET can take place, and light-harvesting of oxadiazole units results in the distinct enhancement of the core emission in higher generations for the dendrimers bearing OXZ units.

### 2.5. Electrochemical properties

Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode cell. For the dendrimers bearing carbazole units, the oxidative sweep is predominated by two reversible peaks originated from the stepwise oxidation (two one-electron transfers) of carbazole units at 0.94 and 1.25 V, and for the dendrimers with oxadiazole units, there is only an irreversible peak at 1.38 V to the one-electron oxidation of oxadiazole units. The oxidative peak for perylene diimide did not appear in all dendrimers, which should be around at 1.60 V versus SCE according to the early reports [38,39]. The HOMO energy values for the dendrimers were calculated relative to ferrocene (Fc), which has a value of −4.8 eV with respect to zero vacuum level. And the optical edge of absorption spectrum is utilized to derive the band gap and give the LUMO energy values for the dendrimers [40]. The measured oxidation potentials (versus reference electrode Ag/AgCl) and HOMO and LUMO energy values for

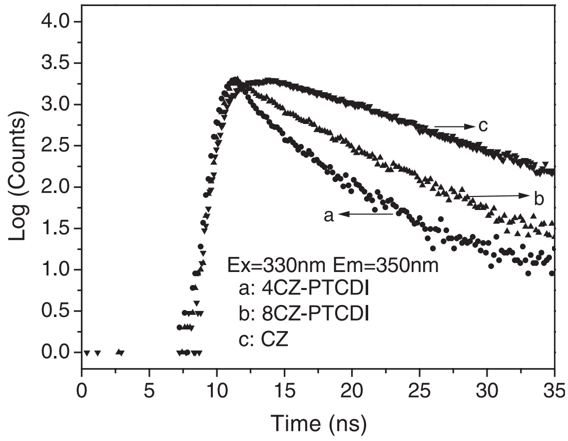


Fig. 11. Carbazole unit fluorescence decay profiles of CZ, 4CZ-PTCDI and 8CZ-PTCDI in $CH_2Cl_2$ ($1.0\times10^{-5}$ M).

Table 2
Fluorescence lifetime data of dendrimers bearing carbazole units and reference compounds in various solvents

| Dendrimers | In THF | | In $CH_2Cl_2$ | | In $C_6H_{12}$ | |
|---|---|---|---|---|---|---|
| | CZ unit[a] (ns) | PTCDI unit[b] (ns) | CZ unit[a] (ns) | PTCDI unit[b] (ns) | CZ unit[a] (ns) | PTCDI unit[b] (ns) |
| CZ | 8.40(100%) | | 6.74(100%) | | 7.68(100%) | |
| PTCDI | | | | 6.49(100%) | | |
| 4CZ-PTCDI | 2.29(43.1%) | 1.04(92.0%) | 2.21(77.5%) | 0.94(55.8%) | | 1.95(25.6%) |
| | 7.46(56.9%) | 2.86(8.0%) | 7.10(22.5%) | 2.14(44.2%) | 7.79(100%) | 5.56(74.4%) |
| 8CZ-PTCDI | 1.43(21.7%) | 1.07(81.9%) | 2.75(45.9%) | 1.27(86.4%) | 1.21(70.4%) | 4.27(46.1%) |
| | 7.26(78.3%) | 4.47(18.1%) | 5.61(54.1%) | 4.84(13.6%) | 6.71(29.6%) | 5.60(53.9%) |

[a] $\lambda_{ex}=330$ nm, $\lambda_{em}=350$ nm.
[b] $\lambda_{ex}=380$ nm, $\lambda_{em}=610$ nm.

dendrimers are summarized in Table 3. It can be seen that there is little effect to the generation variety of dendrimers on the oxidation potential, no distinct shell effect such as redox wave broadening or shift occurred, which can be attributed that the synthesized dendrimers are not large enough to make a global shape [41].

### 2.6. Thermal stability and electroluminescent properties

Dendrimers are generally able to prevent spatial reorientation of molecules, thus eliminating recrystallization tendency and favorably increasing glass transition temperature ($T_g$). Thermal analysis results indicate that such dendron functionalized luminescent materials have good thermal stability, which is very essential for fabricating stable OLEDs. In these dendrimers, the first-generation dendrimers (G-1) have a higher melting point than those of other generation dendrimers (G-0, G-2).

To test these novel dendron-functionalized luminescent materials, single-layer light emitting devices using the dendrimers as the active layer with the structure of ITO//PEDOT//dendrimer//Ba/Al have been fabricated and investigated. The performance data of these devices are collected in Table 4. In results, the device fabricated with dendrimer 2CZ-PTCDI (G-0) has the maximum brightness of 85.4 cd/m$^2$ at 10 V, and the one with dendrimer 8CZ-PTCDI (G-2) has the highest external quantum efficiency of 0.105% (Fig. 12). The turn-on voltage of the G-2 dendrimer based device is about 4 V higher than those of the G-0 and G-1 dendrimer based devices (Figs. 13 and 14), suggesting that the larger dendron shell has a larger influence on the trapping process [9]. In all devices, EL emission peaks at about 650 nm (Fig. 15) are similar to PL spectra of corresponding dendrimers in thin film (Fig. 2), indicating that EL emission has the same recombination zone as PL. Also it hints that the recombination of excitons in our fabricated EL devices is not close to cathode or anode vicinity, otherwise EL emission will be affected by electrodes. In the case of single-layer EL device, the emission is under the influence of electrode vicinity in that the emission layer is directly contacted with electrodes without buffer layer. It might be the site-isolation contribution of dendron wedges, which can efficiently prevent the core luminorphores from approaching electrodes. The EL mechanism can be suggested as follows: electrons are injected from the cathode (2.8 eV) to LUMO orbital of the perylene diimide moiety (3.9 eV), and holes

Table 3
Oxidation potentials and calculated HOMO and LUMO energies for the dendrimers

| Dendrimers | $E_{ox}$ (V versus Ag/AgCl)[a] | HOMO (eV) | LUMO (eV) |
|---|---|---|---|
| 2CZ-PTCDI | 0.94 | −5.22 | −3.23 |
| 4CZ-PTCDI | 0.94 | −5.22 | −3.25 |
| 6CZ-PTCDI | 0.94 | −5.22 | −3.25 |
| 8CZ-PTCDI | 0.94 | −5.22 | −3.25 |
| 2OXZ-PTCDI | 1.37 | −5.65 | −3.64 |
| 4OXZ-PTCDI | 1.38 | −5.66 | −3.66 |
| 6OXZ-PTCDI | 1.38 | −5.66 | −3.66 |
| 2Ph-PTCDI | 1.62[b] | −5.90 | −3.90 |

[a] The oxidative potential of reference ferrocene (Fc) versus reference electrode Ag/AgCl is 0.52 V.
[b] The oxidative potential of reference compound perylene diimide (2Ph-PTCDI) is according to the early reports [38,39].

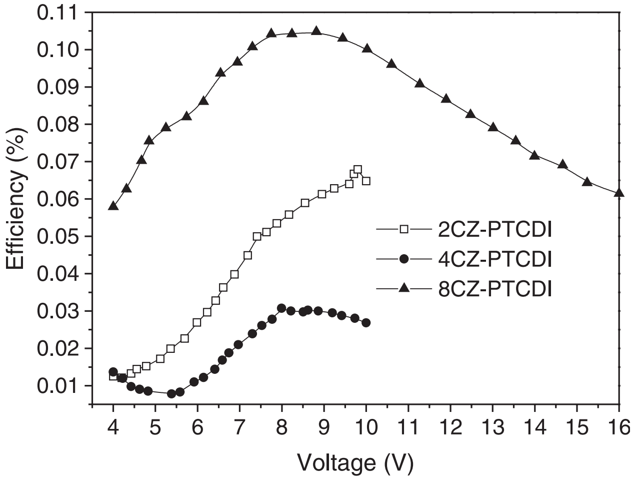


Fig. 12. Efficiency–voltage characteristics of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI based OLEDs with structure of ITO//PEDOT//dendrimer//Ba/Al.

Table 4
EL performances of device based on dendrimers

| EL device structure | Voltage/V @QEmax | Current (mA/cm$^2$) | Luminance (cd/m$^2$) | Eff (%) | EL peak ($\lambda_{max}$/nm) |
|---|---|---|---|---|---|
| ITO//PEDOT(80 nm)//2CZ-PTCDI(100 nm)//Ba (4 nm)/Al(160 nm) | 9.8 | 379.4 | 85.4 | 0.069 | 650 |
| ITO//PEDOT(80 nm)//4CZ-PTCDI(70 nm)//Ba (4 nm)/Al(160 nm) | 8.0 | 1.4 | 29.8 | 0.031 | 650 |
| ITO//PEDOT(80 nm)//8CZ-PTCDI(90 nm)//Ba (4 nm)/Al(160 nm) | 8.5 | 2.37 | 39.8 | 0.105 | 650 |

are also injected from ITO (4.6 eV) to PEDOT layer (5.1 eV). Then the holes are transferred to HOMO orbital of the carbazole moiety (5.2 eV) and perylene diimide moiety (5.9 eV) in turn. Finally the holes and electrons are trapped in perylene diimide moiety to form exciton that undergoes radiative decay, resulting in the perylene diimide characteristic emission [42–44]. Obviously, the peripheral of carbazole unit did not emit light in the operation of the devices. It is believed that the carbazole unit reduces the hole-injection barrier by 0.7 eV from 5.9 eV (HOMO orbital energy of core perylene diimide) to 5.2 eV (HOMO orbital energy of carbazole unit), thus facilitating hole injection from ITO electrode (Table 3). Similarly, the high electron affinity oxadiazole unit is helpful to electron injection. Therefore, incorporating such peripherally functional units can realize tuning carrier injection as demonstrated in above-mentioned single layer EL device, in which both the traditional electron and hole transporting layers are subtracted. Also, it should be pointed out that the pure dendrimers used as host emitter without any matrix is paving a way or allow to fabricate EL devices with printing techniques.

## 3. Experimental

Melting points were measured on a X4 micro melting point apparatus. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-500 spectrometer. MS were recorded on ESI or MALDI-TOF mass spectroscopy using $\alpha$-cyano-4-hydroxycinnamic acid as a matrix. Glass-transition temperatures ($T_g$) were measured using a differential scanning calorimeter TA DSC 2910 instrument at a scan rate of 10 °C/min. Absorption and fluorescence spectra were recorded on a Varian Cary 500 and a Varian Cary Eclipse, respectively.

Cyclic voltammetry (CV) measurements were carried out on a CHI 800 electrochemical instrument using millimolar solutions in $CH_2Cl_2$ containing 0.1 M of the support electrolyte of tetrabutylammonium perchloride with a three-electrode cell and potentiostat assembly. A platinum electrode was used as the working electrode and the reference electrode was Ag/AgCl electrode (KCl saturated). The potentials were measured at the scan rate of 100 mV/s, and each measurement was calibrated with an

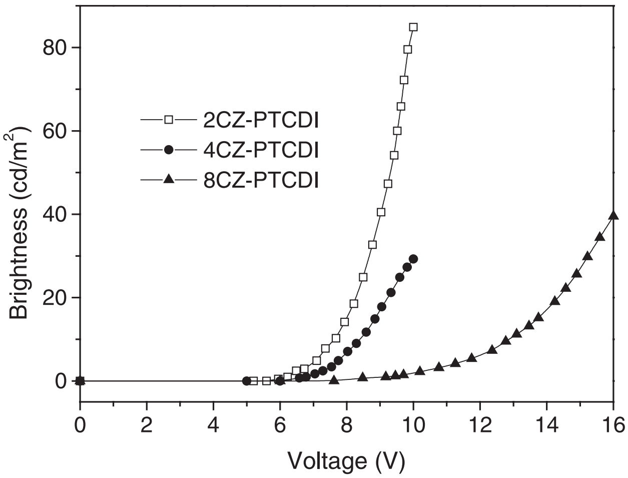


Fig. 13. Light–voltage characteristics of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI based OLEDs with structure of ITO//PEDOT//dendrimer//Ba/Al.

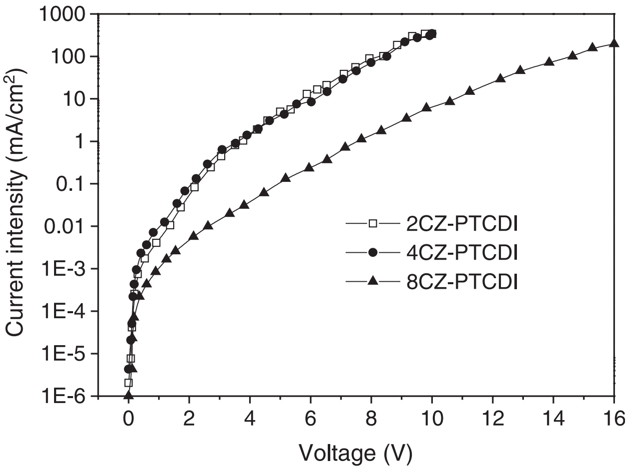


Fig. 14. Current–voltage characteristics of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI based OLEDs with structure of ITO//PEDOT//dendrimer//Ba/Al.

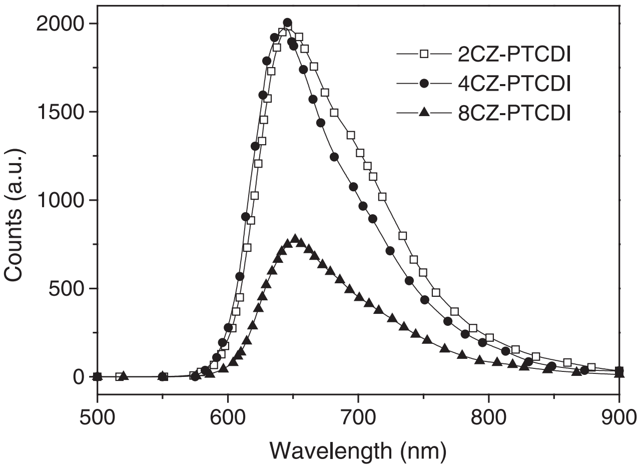


Fig. 15. Electroluminescence spectra of 2CZ-PTCDI, 4CZ-PTCDI and 8CZ-PTCDI based OLEDs with structure of ITO//PEDOT//dendrimer//Ba/Al.

internal standard of the ferrocene/ferrocenium ($Fc/Fc^+$) redox system.

OLEDs are prepared according to the following standard procedure: ITO coated glass substrates were cleaned via repeated ultrasonic washing and oxygen plasma treating. The buffer layer was spin-coated from the aqueous dispersion of poly(3,4-ethylenedioxythiophene) (PEDOT) (Bayer AG). The active dendrimer layer of 2CZ-PTCDI was spin-coated from 1.2 wt% toluene/chloroform solution, and 4CZ-PTCDI, 8CZ-PTCDI from 2 wt% chlorobenzene solution and 1.9 wt% toluene/THF solution, respectively. The cathode layer of Ba (4 nm)/Al (160 nm) was thermally evaporated in a vacuum chamber (pressure $<3\times10^{-4}$ Pa). The thickness of different layers was measured by Tencor R-step 500 surface-profiler. The *I–V* and *L–V* characteristics were measured with a computer-controlled source meter Keithley 236 and Si-photodiode calibrated by an integrating sphere. The EL spectra were recorded on an Oriel CCD spectrograph.

The fluorescence lifetime study was performed by an Edinburgh FL 900 single-photon counting system. Data were analyzed using a non-linear least-squares fitting program, with deconvolution of the exciting pulse being $\sim$200 ps.

## 4. Conclusions

Three generations of a series of dendrimers for red-light emission have been successfully synthesized, which contain perylene diimide cores, Fréchet-type poly(benzyl ether) dendrons, and peripheral functional units such as carbazole or oxadiazole. The peripheral chromophores oxadiazole have specific light-antenna and enhanced core luminescence property. The light-harvesting for the chromophore luminescence by the light antenna can be more efficient than the direct excitation of core perylene diimide. In solid state, the higher generation dendrimer has the site-isolation or dendron-dilution effect to a certain extent. All three-generation dendrimers have good solubility and thermal stability. The preliminary EL results of single-layer devices made with these dendrimers demonstrate that they could be applied as a promising active red luminescent emitter with carrier-transporting ability in OLEDs.

## Acknowledgements

This study was partly supported by Natural Science Foundation of China, Education Committee of Shanghai and Scientific Committee of Shanghai. We also thank Prof Chen-Pin Chang in Fu Jen University/Taiwan for the fluorescent lifetime measurements.

## References

[1] Chen CT, Chiang CL, Lin YC, Chan LH, Huang CH, Tsai ZW, et al. Org Lett 2003;5:1261.
[2] Okamoto T, Terada E, Kozaki M, Uchida M, Kikukawa S, Okada K. Org Lett 2003;5:373.
[3] Huang F, Hou L, Wu H, Wang X, Shen H, Cao W, et al. J Am Chem Soc 2004;126:9845.
[4] Miteva T, Meisel A, Knoll W, Nothofer HG, Scherf U, Müller DC, et al. Adv Mater 2001;13:565.
[5] Tonzola CJ, Alam MM, Bean BA, Jenekhe SA. Macromolecules 2004;37:3554.
[6] Ma DG, Lupton JM, Beavington R, Burn PL, Samuel IDW. Adv Funct Mater 2002;12:507.
[7] Brousmiche DW, Serin JM, Fréchet JMJ, He GS, Lin TC, Chung SJ, et al. J Am Chem Soc 2003;125:1448.
[8] Lo SC, Male NAH, Markham JPJ, Magennis SW, Burn PL, Salata OV, et al. Adv Mater 2002;14:975.
[9] Qu JQ, Zhang JY, Grimsdale AC, Müllen K, Jaiser F, Yang XH, et al. Macromolecules 2004;37:8297.
[10] Wang BB, Zhang X, Jia XR, Luo YF, Sun Z, Yang L, et al. Polymer 2004;45:8395.
[11] Astruc D, Chardac F. Chem Rev 2001;101:2991.
[12] Grabchev I, Bojinov V, Chovelon JM. Polymer 2003;44:4421.
[13] Wang PW, Liu YJ, Devadoss C, Bharathi P, Moore JS. Adv Mater 1996;8:237.
[14] Devadoss C, Bharathi P, Moore JS. J Am Chem Soc 1996;118:9635.
[15] Adronov A, Gilat SL, Fréchet JMJ, Ohta K, Neuwahl FVR, Fleming GR. J Am Chem Soc 2000;122:1175.
[16] Gilat SL, Adronov A, Fréchet JMJ. Angew Chem Int Ed 1999;38:1422.
[17] Freeman AW, Koene SC, Malenfant PRL, Thompson ME, Fréchet JMJ. J Am Chem Soc 2000;122:12385.
[18] Furuta P, Brooks J, Thompson ME, Fréchet JMJ. J Am Chem Soc 2003;125:13165.
[19] Lupton JM, Samuel IDW, Beavington R, Frampton MJ, Burn PL, Bässler H. Phys Rev B 2001;63:155206.
[20] Kwok CC, Wong MS. Macromolecules 2001;34:6821.
[21] Kwok CC, Wong MS. Chem Mater 2002;14:3158.
[22] Du P, Zhu WH, Xie YQ, Zhao F, Ku CF, Cao Y, et al. Macromolecules 2004;37:4387.
[23] Park JS, Lee CW, Gong MS. Synth Met 2003;132:177.
[24] Tian H, Liu PH, Zhu WH, Gao EQ, Wu DJ, Cai SM. J Mater Chem 2000;10:2708.

[25] Qu JQ, Pschirer NG, Liu DJ, Stefan A, Schryver FCD, Müllen K. Chem Eur J 2004;10:528.

[26] Sugiyasu K, Fujita N, Shinkai S. Angew Chem Int Ed 2004;43:1229.

[27] Hawker CJ, Fréchet JMJ. J Am Chem Soc 1990;112:7638.

[28] Hawker CJ, Wooley KL, Fréchet JMJ. J Chem Soc Perkin Trans 1 1993;1287.

[29] Thomas KRJ, Thompson AL, Sivakumar AV, Bardeen CJ, Thayumanavan S. J Am Chem Soc 2005;127:373.

[30] Lor M, Viaene L, Pilot R, Fron E, Jordens S, Schweitzer G, et al. J Phys Chem B 2004;108:10721.

[31] Onodera H, Araki Y, Fujitsuka M, Onodera S, Ito O, Bai FL, et al. J Phys Chem A 2001;105:7341.

[32] Förster T. Ann Phys 1948;2:55.

[33] Dexter DL. J Chem Phys 1953;21:836.

[34] Yang SJ, Tian H. Trends Photochem Photobiol 2002;9:55.

[35] Choi MS, Aida T, Luo HX, Araki Y, Ito O. Angew Chem Int Ed 2003;42:4060.

[36] Serin JM, Brousmiche DW, Fréchet JMJ. Chem Commun 2002;2605.

[37] Serin JM, Brousmiche DW, Fréchet JMJ. J Am Chem Soc 2002;124:11848.

[38] Lee SK, Zu YB, Herrmann A, Geerts Y, Müllen K, Bar AJ. J Am Chem Soc 1999;121:3513.

[39] Parra V, Caňo TD, Rodriguez-Méndez ML, Saja JAD, Aroca RF. Chem Mater 2004;16:358.

[40] Hohle C, Hofmann U, Schloter S, Thelakkat M, Strohriegl P, Haarer D, et al. J Mater Chem 1999;9:2205.

[41] Satoh N, Cho JS, Higuchi M, Yamamoto K. J Am Chem Soc 2003;125:8104.

[42] Tao XT, Zhang YD, Wada T. Adv Mater 1998;10:226.

[43] Ding LM, Karasz FE, Lin Y, Pang Y, Liao L. Macromolecules 2003;36:7301.

[44] Hou Q, Zhou QM, Zhang Y, Yang W, Yang RQ, Cao Y. Macromolecules 2004;37:6299.