Dendron-Functionalized Macromolecules: Enhancing Core Luminescence and Tuning Carrier Injection

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ABSTRACT: A novel series of naphthalimide dendrimers has been synthesized based on a convergent and divergent combined approach. The dendrimers consist of naphthalimide-based cores, Fréchet-type poly(aryl ether) dendrons, and carbazole (CZ) or oxadiazole (OXZ) peripheral groups. The higher generation dendrimer has site-isolation effect, or the dilution effect of the dendrons. This configuration would reduce the aggregating extent or possibility of the core unit, thus resulting in a relatively small red-shift of absorption and fluorescent spectra when they form a solid film for the applications. Studies of steady-state fluorescence properties of the dendrimers show that excitation of the terminal chromophores results mainly in the core emission alone, as the donor emission is seriously quenched due to its effective Förster intramolecular energy transfer to the core. The dendrimers show enhanced luminescence properties of the core, and the enhanced luminescent efficiency is dependent on the generation number of the dendrimers. Time-resolved luminescent measurements further supported the conclusion that the contribution tendency for each peripheral donor is decreased with the increasing of the generation number, especially for the third generation. The dendron-incorporated carbazole unit can decrease the HOMO orbital energy by 0.4 eV, thus facilitating the hole-injection in electroluminescent (EL) devices. The preliminary EL results with a single-layer architecture made with the dendrimers by means of the spin-coating technique demonstrate that these dendrimers could be utilized as promising active nondoping emitters.

Introduction

Research on novel luminescent materials has played an important role in developing organic light-emitting diodes (OLEDs). Both small molecules[1] and polymers[2] have been studied extensively for use in OLEDs. Recently, several research groups have investigated some well-defined dendrimers as an alternative class of electroluminescent (EL) materials.[3] In contrast to polymers, the beauty of dendrimers is that their size and architecture can be specifically controlled in their synthesis.[4] The dendritic architecture can be also used to improve the solubility of luminescent chromophores to form a uniform film with the spin-coating technique, thus overcoming the high cost of the vacuum deposition process.[5]

A characteristic of dendritic macromolecules is the presence of numerous peripheral chain ends that all surround a single core. The globular shape of dendrimers provides a large surface area that can be decorated with the chromophores, thus resulting in a large absorption cross section and enabling efficient capture of photons.[6] Furthermore, both the peripheral chromophores and the focal dye (or core) are capable of contributing the absorption of the entire macromolecule. In a dendritic antenna, the peripheral donor units collect photons and transfer the excitation energy through space to the core or focal point acceptor chromophores, that is, dendrons act as the “molecular lens”.[7] For example, Fréchet et al.[8] reported poly(aryl ether) dendrimers, in which coumarin 2 acts as a light-harvesting antenna and coumarin 343 as a focal chromophore acceptor. In the phenyl acetylene dendrimers reported by Moore and co-workers, there is an energy gradient from the periphery toward the center.[9]

Luminescent dendrimers consists of three main units: the emissive core, the dendrons, and the terminal or periphery groups. This modular construction enables the processing and electronic properties to be tuned independently. Dendrimers provide new opportunities for precisely placing some charge-carrier transporting units by the generation in a three-dimensional nanoscale construction. Despite the impressive scope of controlling solubility and amorphous form,[7] examples of the design of modulating charge carrier-transporting dendron-function of a dendrimer for OLED applications so far are rare. Here we report a novel series of naphthalimide-based dendrimers (shown in Scheme 1), into which the dendron periphery group carbazole or oxadiazole is introduced to design charge carrier transporting tunable type emitters for OLEDs. These dendrimers show specific light-antenna capacity and tunable charge carrier-transporting characteristics. Specifically, the enhanced emission for the dendrimers were observed comparing with that of a direct-core emission, that is, light harvest for the luminescence of the chromophore by the light antenna is more efficient than direct excitation at the absorption maximum by an external light source. Time-resolved luminescence measurements have been done for the dendrimers to reveal the interaction between the donors and the core.

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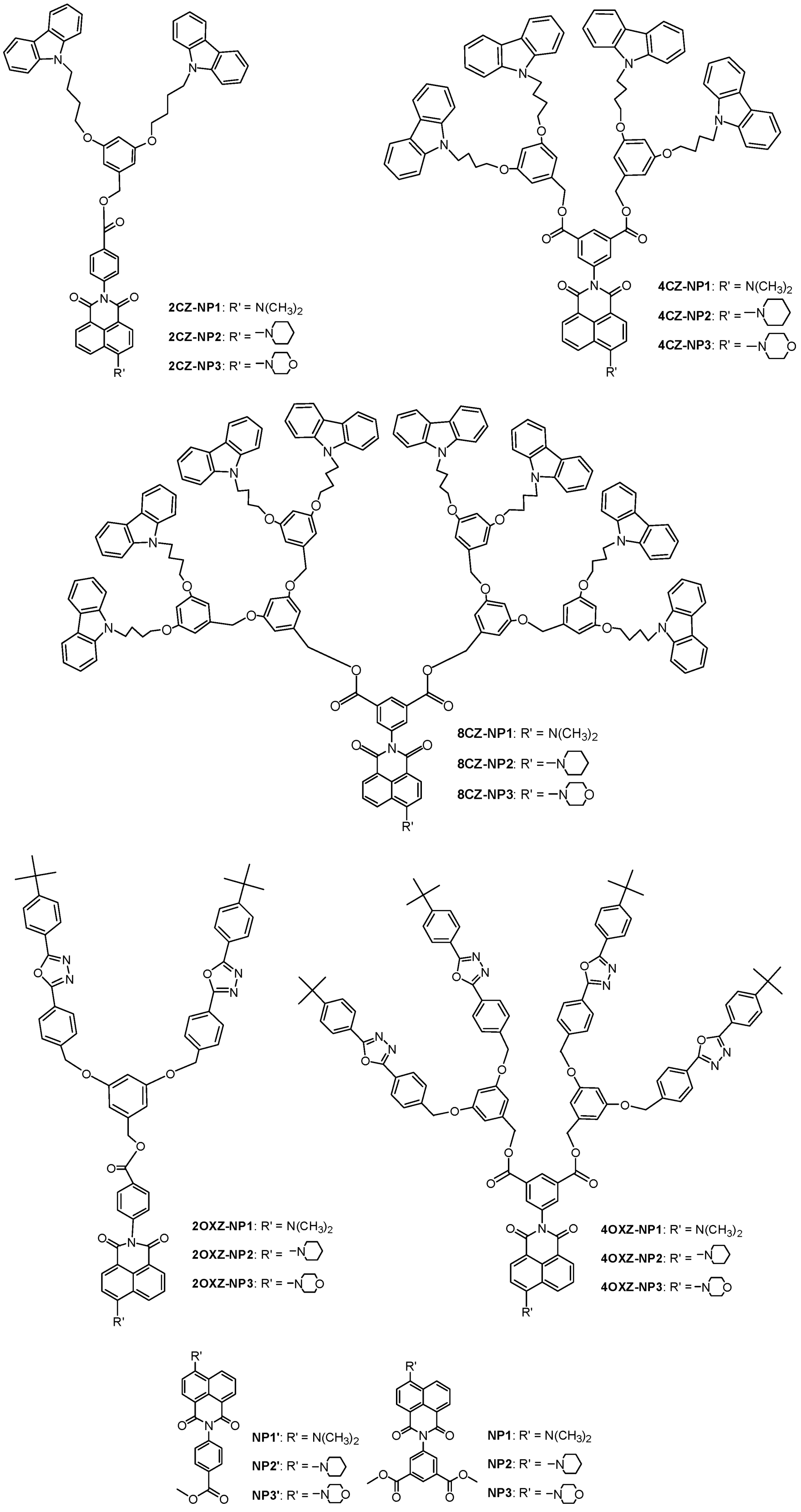
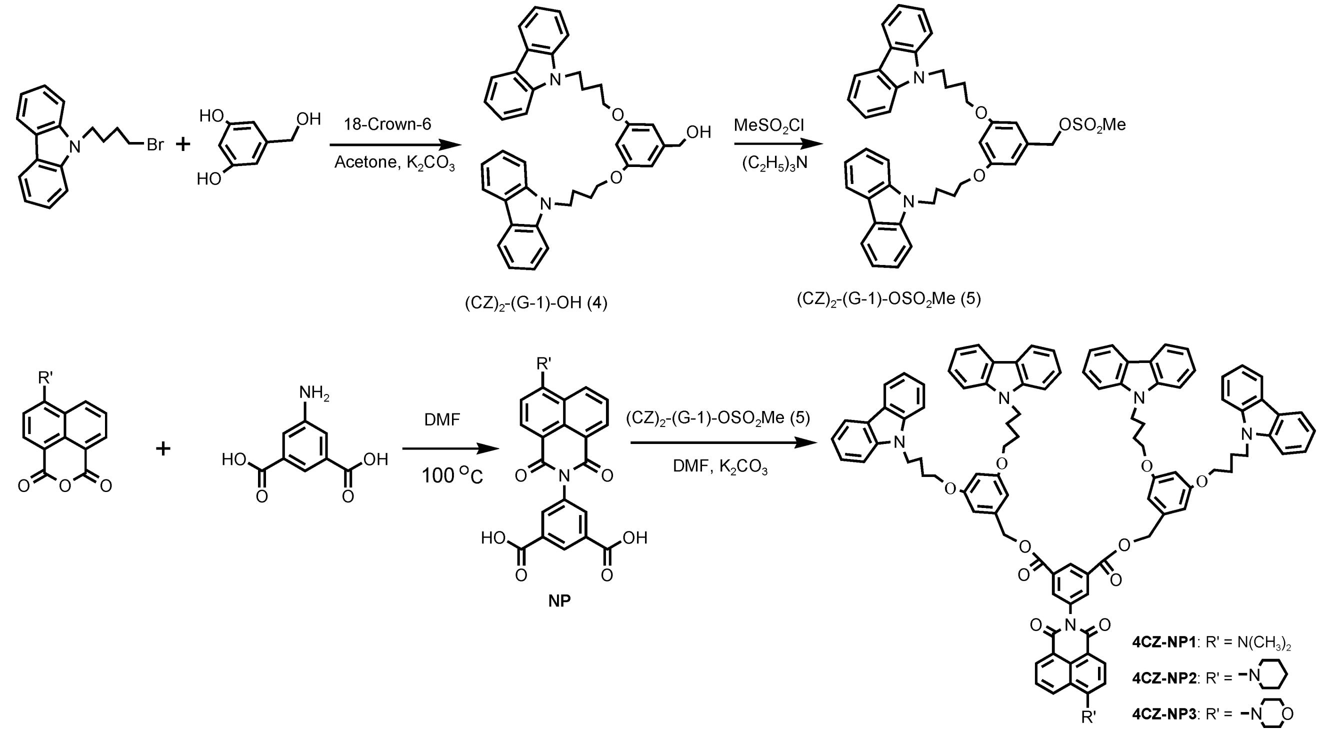
Scheme 1. Chemical Structures of Target Dendrimers and the Reference Compounds



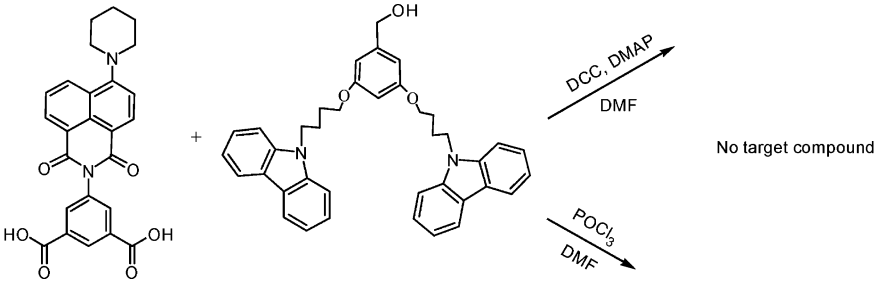
Results and Discussion

Design and Synthesis of Light-Emitting Dendrimers. To study the properties of site-isolation and light harvesting, the synthesized dendrimers features the naphthalimide chromophore at the center of the dendrimer with a specific functional periphery constructed by Fréchet-type poly(aryl ether) dendrons (shown in Scheme 1). We chose 1,8-naphthalimide (NP) as a fluorescent core because of its chemical stability and high fluorescent efficiency, whose derivatives are known to be acted as the promise triplet host matrix,[10] supramolecular moieties for the study of photoinduced

Scheme 2. Synthetic Route of Second-Generation Dendrimers 4CZ-NPm



Scheme 3. Attempt to Synthesize Target Dendrimers Using both Conventional Synthetic Ester Protocols and Methods without Tosylation Activation



electron transfer,[11] fluorescence switches,[12] liquid crystal displays,[13] and EL materials.[14] The functional periphery of the dendrimers is carbazole (CZ) or oxadiazole (OXZ) units that can play a major role in charge carrier-transporting and also act as energy donors (light antenna) for the core acceptor chromophores. A combination of divergent and convergent steps, also known as the double-stage convergent approach,[15] can be specifically developed to synthesize the dendrimers nCZ-NPm (n = 2, 4, 8; m = 1, 2, 3) and nOXZ-NPm (n = 2, 4; m = 1, 2, 3). NPm serves as a molecular core unit that bears two acid groups. Such reactivity polarity is reversed to the "classical" convergent synthesis of polyether dendrimers originally reported by Hawker and Fréchet.[16] Coupling two CZ or OXZ units, which will become the terminal groups, to 3,5-dihydroxybenzyl alcohol occurred readily in the presence of potassium carbonate and 18-crown-6 in acetone when heated at reflux. This gave the first-generation dendron alcohol (CZ)$_2$-(G-1)-OH or (OXZ)$_2$-(G-1)-OH. To illustrate this case, the synthesis of 4CZ-NP3 by the convergent growth approach is shown in Scheme 2. Reaction of 9-(4-bromobutyl)-9*H*-carbazole with 3,5-dihydroxybenzyl alcohol yielded (CZ)$_2$-(G-1)-OH, followed by tosylation at ambient temperature to give the second-generation dendron (CZ)$_2$-(G-1)-OSO$_2$Me. The bromination of the benzyl alcohol group at the focal point of (CZ)$_2$-(G-1)-OH by reaction with carbon tetrabromide/triphenylphosphine proceeded smoothly to afford the corresponding bromide (CZ)$_2$-(G-1)-Br. Reaction of 2.1 equiv of (CZ)$_2$-(G-1)-Br with 3,5-dihydroxybenzyl alcohol gave (CZ)$_4$-(G-2)-OH, which when reacted with methane sulfonyl chloride gave the third-generation dendron (CZ)$_4$-(G-2)-OSO$_2$Me. In the presence of potassium carbonate in DMF at 100 °C, assembly of the core intermediate with the corresponding different generation dendrons was achieved to obtain the final dendrimers. Similarly, we prepared other target dendrimers.

It should be pointed out that the activation step of tosylation is very critical to make the coupling possible and successful. Using conventional synthetic ester protocols and methods (shown in Scheme 3), attempts to prepare target dendrimers failed. The dendrons and the dendrimers were characterized by ^{1}H NMR, ^{13}C NMR, and FAB or MALDI−TOF mass spectroscopy. With the dendron generation increasing, ^{1}H NMR and ^{13}C NMR signals become more complicate and difficult to discern structures. To assess more clearly the identity of chemical structures, further characterization has been performed by MALDI−TOF mass spectroscopy, which has become very valuable for macromolecules (MW > 1500).[7] All of the third generation of dendrimers show the corresponding ion peaks of $M^+ + Na$ and $M^+ + K$ (Figure 1). The charge-state determination for

Table 1. Absorption and Fluorescence Emission Spectral Data in THF and Solid Film for Target Dendrimers and Melting Points

		in THF			in solid film		
dendrimers	mp/°C	λ^{abs}_{max} (nm) (log ϵ)	λ^{em}_{max}/nm	η^{a} (%)	LER^{b} (λ_{ex} (nm))	λ^{abs}_{max} (nm)	λ^{em}_{max} (nm)
2OXZ-NP1	149−150	295 (4.89), 411 (4.12)	355, 514	94	4.8 (295)	317, 436	542
2OXZ-NP2	154−155	296(4.92), 400 (4.1)	355, 516	88	5.1 (296)	318, 421	537
2OXZ-NP3	168−170	296(1.92), 391 (4.09)	355, 511	91	6.7 (296)	318, 415	527
4OXZ-NP1	196−198	296 (5.26), 411 (4.02)	355, 514	96	11.9 (296)	315, 424	
4OXZ-NP2	172−173	296 (5.28), 406 (4.06)	355, 521	98	12 (296)	314, 410	534
4OXZ-NP3	195−196	296 (5.28), 393 (4.14)	355, 513	98	16.3 (296)	319, 400	527
2CZ-NP1	136−137	330 (4.09), 345 (4.15) 411 (4.17)	351,366, 514	87	3.6 (330), 3.5 (345)	333, 432, 348	537
2CZ-NP2	136−138	330 (4.14), 345 (4.20), 406 (4.24)	351,366, 521	92	3.6 (330), 3.3 (345)	333, 424, 348	534
2CZ-NP3	150−151	330 (4.0), 345 (4.11), 393 (4.06)	351,366, 513	93	2.8 (330), 2.4 (345)	333, 418, 348	522
4CZ-NP1	144−145	330 (4.26), 345 (4.34) 411 (4.11)	351, 366, 514	94	5.8 (330), 5.7 (345)	333, 426, 348	537
4CZ-NP2	139−140	330 (4.37), 345 (4.33) 406 (4.19)	351, 366, 521	95	5.4 (330), 5.0 (345)	333, 413, 348	531
4CZ-NP3	194−195	330 (4.29), 345 (4.36), 393 (4.11)	351, 366, 513	96	5.4 (330), 4.2 (345)	333, 406, 348	519
8CZ-NP1	107−109	330 (4.49), 345 (4.53), 411 (3.94)	351, 366, 514	84	5.7 (330), 5.6 (345)	333, 426, 348	528
8CZ-NP2	115−117	330 (4.45), 345 (4.51), 406 (4.01)	351, 366, 521	89	5.0 (330), 4.4 (345)	333, 413, 348	531
8CZ-NP3	116−118	330 (4.46), 345 (4.53), 393 (4.0)	351, 366, 513	90	5.4 (330), 4.0 (345)	333, 405, 348	518

[a] Peripheral donor emission quenching efficiency (η) was calculated by comparing the integration of donor emission between the simple mixture and the target dendrimer excited at corresponding donor absorption peak when these two spectra are normalized at the λ_{max} value of the core chromophore. [b] The core luminescence enhancing ratio (LER) was calculated by comparing the integration of acceptor emission between the simple mixture and the target dendrimer excited at corresponding donor absorption peak when these two spectra are normalized at the λ_{max} value of the core chromophore.

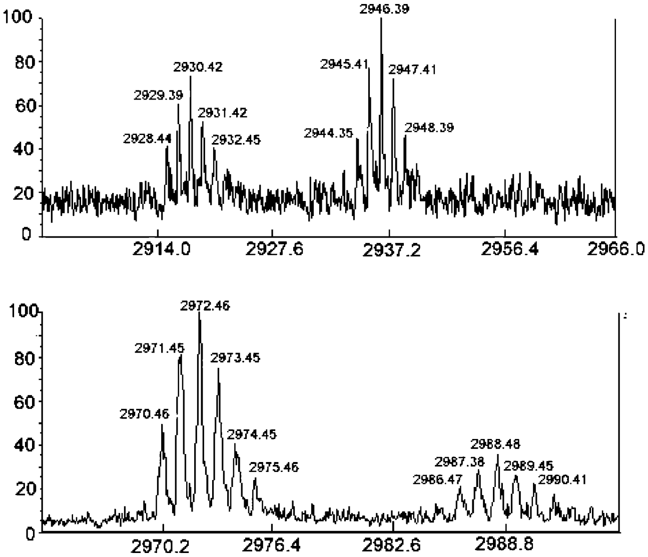


Figure 1. MALDI−TOF mass spectra of dendrimers 8CZ-NP1 (top) and 8CZ-NP3 (bottom).

isotropic distributions with peak separation of 1.0 was performed by high-resolution scan experiments. A peak at m/z 2930.42 for 8CZ-NP1 ascribed to $M^+ + Na$ has been observed. Another centered at 2946.39 with higher abundance for 8CZ-NP1 corresponds to $M^+ + K$.

Light-Harvesting and Enhanced Luminescence Properties. The absorption and emission spectral data of the dendrimers are listed in Table 1. In THF, the absorption peaks at about 330 and 345 nm are attributed to the absorption of the carbazole moiety; the absorption peak at 296 nm is attributed to the OXZ moiety. The absorption peaks characterized for naphthalimide unit NP1, NP2, and NP3 are located at 411, 406, and 393 nm, respectively. The dendrimers nCZ-NPm (n = 2, 4, 8) show very similar absorption characteristics in THF, as shown in Figure 2. In solid neat film, the CZ moiety of 2CZ-NPm, 4CZ-NPm, and 8CZ-NPm also shows similar absorption characteristics (Figure 3). In contrast to the absorption in the solution, the absorption of core chromophores NP1, NP2, and NP3 in solid film shifts bathochromically due to the aggregation effect. However, the red-shift in the absorption spectra is greatly dependent on the dendrimer generation number. For instance, compared with their absorption in the solution, the absorption red shifts of 2CZ-NP3, 4CZ-NP3, and 8CZ-NP3 are 25, 13, and 12 nm, respectively. It can be concluded that the higher generation dendrimer has a site-isolation effect or a dilution effect due to the dendrons. This configuration

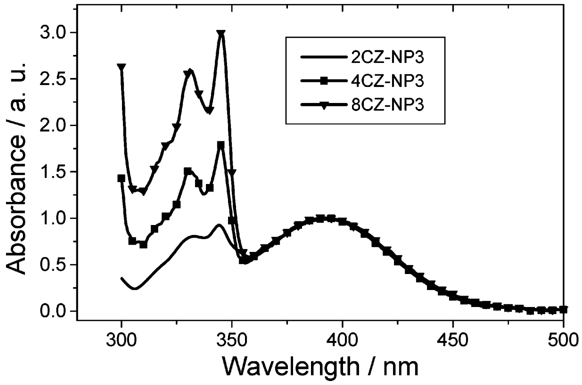


Figure 2. Absorption spectra of 8CZ-NP3, 4CZ-NP3, and 2CZ-NP3 in THF (2.4 × 10^{-5} mol·L^{-1}), normalized at the absorption peak of naphthalimide unit.

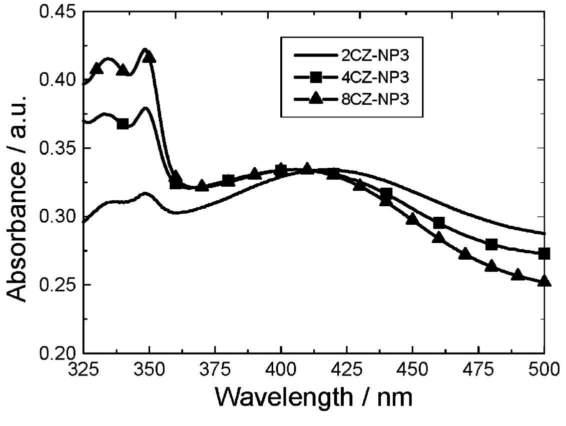


Figure 3. Normalized absorption spectra of 2CZ-NP3, 4CZ-NP3, and 8CZ-NP3 in solid film. Note: the absorbance of carbazole unit disproportional to the generation and the number of carbazole is attributed to the thickness difference of the inhomogeneous film samples.

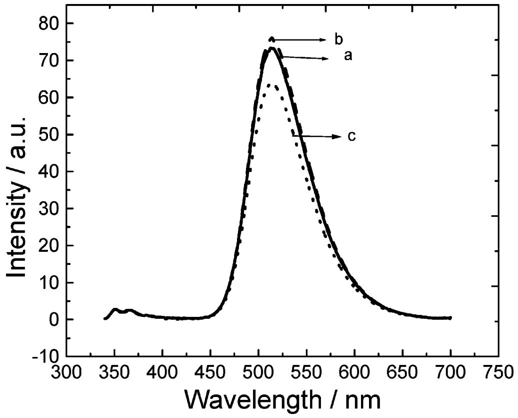


Figure 4. Emission spectra of 4CZ-NP3 in THF (2.4 × 10^{-5} mol·L^{-1}) at excitation of (a) the dendrimer periphery CZ (330 nm), (b) the dendrimer periphery CZ (345 nm), and (c) the core (393 nm). The relative fluorescent intensities for the core: 1.16, 1.20, and 1.00, respectively.

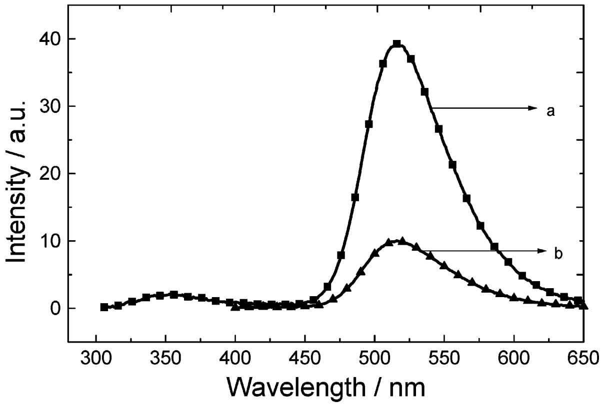


Figure 5. Emission spectra of 4OXZ-NP3 in THF (3.0 × 10^{-6} mol·L^{-1}) at the excitation of (a) the dendrimer periphery OXZ (296 nm) and (b) the core (393 nm). The relative fluorescent intensities for the core are 3.9 and 1.0, respectively.

would reduce the aggregating extent or possibility of the core unit, thus resulting in a relatively small red-shift of absorption and fluorescent spectra when the solid film is formed for the applications.

Dendrimers have an ideal architecture to study the interaction between the chromophores. The reference carbazole that lacks the acceptor focal dye shows two strong emission peaks at 351 and 363 nm excited at 330 nm. However, the excitation of the peripheral donor units (carbazole or oxadiazole) of the dendrimers in this work mainly results in the fluorescence of the core dye alone (Figures 4 and 5). Actually, the emission intensity of the core for 4CZ-NP3 excited at peripheral group (345 nm) is about 20% higher than that of the direct core excitation (393 nm). Similarly as shown in Figure 5, the emission intensity of the core for 4OXZ-NP3 excited at the peripheral group (296 nm) is 3.9 times higher than that of the direct core excitation (393 nm). The intensity of the harvested emission for the dendrimers synthesized in this work is stronger than that of the direct-core emission; that is, light harvest for the luminescence of the chromophore by the light antenna is more efficient than direct excitation at the absorption maximum by an external light source.[17] A similar effect has already been described for coumarin-labeled dendrimers[18] as well as for phenyl acetylene dendrimers that bear a focal perylene chromophore.[19]

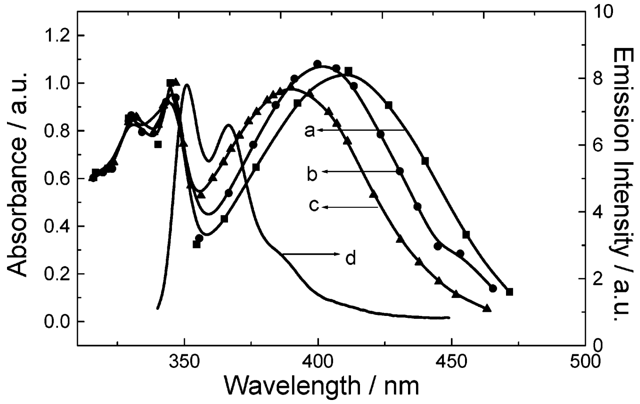


Figure 6. Absorption spectra of compounds 2CZ-NP1 (curve a), 2CZ-NP2 (curve b), and 2CZ-NP3 (curve c) and emission spectra of $(CZ)_2$-(G-1)-OH (curve d) in THF (2.4 × 10^{-5} mol·L^{-1}) excited at 330 nm. It indicates that there exists an overlap between the emission band of the donor and the absorption band of the acceptor, resulting in Förster energy transfer (FRET) occurring from a carbazole unit to the core naphthalimide.

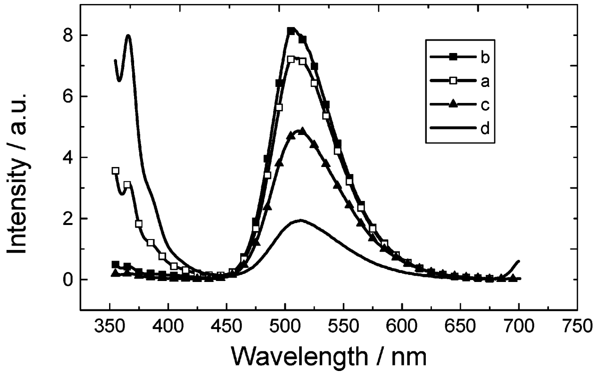


Figure 7. Emission spectra in THF (2.4 × 10^{-5} mol·L^{-1}) of (a) 8CZ-NP3, (b) 4CZ-NP3, (c) 2CZ-NP3, and (d) a simple mixture of $(CZ)_2$-(G-1)-OH and NP3 (molar ratio = 2:1) at an excitation of 345 nm.

The light harvesting and the enhanced luminescence properties of the core might be explained by the interaction between the core chromophore and the terminal groups. The excitation spectra of the dendrimers clearly indicate that the fluorescence of the core naphthalimide unit results not only from the contribution of itself but also from that of the peripheral carbazole or oxadiazole units. The optical properties of each interactive component are illustrated using first-generation dendrimers 2CZ-NP1, 2CZ-NP2, 2CZ-NP3, and $(CZ)_2$-(G-1)-OH (as shown in Figure 6), and there exists an overlap between the emission band of the donor and the absorption band of the acceptor, thus creating a pathway for Förster resonance energy transfer (FRET) to occur from the carbazole unit to the core naphthalimide. Figure 7 shows the relative emission intensity for different generation dendrimers 2CZ-NP3, 4CZ-NP3, and 8CZ-NP3 when excited at 345 nm. Comparing with that of the simple mixture containing peripheral donor and the core dye, the core emission of all dendrimers increased. The fluorescent intensity of 4CZ-NP3 is strongest, where a 4.2-fold increase in the core emission relative to the emission of the core lacking the peripheral donors, a 4.0-fold increase in the core emission in 8CZ-NP3, and a 2.4-fold enhancement of the core emission in 2CZ-NP3 were observed. The emission of the donor CZ was drastically decreased, and the fluorescent quenching

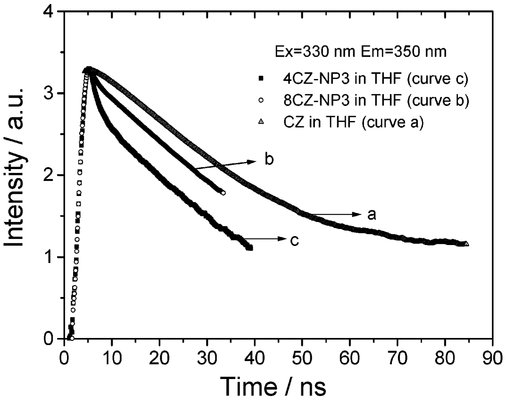


Figure 8. Fluorescence decay profiles of the compounds in THF (1 × 10^{-5} mol·L^{-1}): (a) CZ, (b) 8CZ-NP3, and (c) 4CZ-NP3 at 350 nm upon excitation at 345 nm.

reached higher than 84%. If one considers the number of peripheral donors in different generation dendrimers, the core luminescence-enhancing ratio for the contribution of each donor CZ unit in 2CZ-NP3, 4CZ-NP3, and 8CZ-NP3 is 1.2, 1.04 and 0.5, respectively. It can be demonstrated that the energy transfer efficiency is highly dependent on the dendrimer generation number. That is, with the dendrimer generation number increasing, the contribution tendency of each CZ unit for the core luminescence enhancement decreased, especially for the third generation. This might be explained in terms of the Förster mechanism. Since Förster transfer is a resonant dipole coupling process that transfers energy between singlet states and conserves the spin state of the donor and the acceptor chromophores,[20] it is known that the efficiency of Förster energy transfer decreases as the inverse sixth power dependence on the donor–acceptor separation. Generally, the higher the number of donor peripheral groups that surround the core, the larger the cross-section for energy collection. However, the average distance between the core and the peripheral donor groups also increases as the generation number increases. Therefore, dendrimer generation number determines the Förster energy transfer efficiency of the donor CZ to the core. The luminescence-enhancing ratios of other dendrimers are summarized in Table 1 and show a very similar tendency.

It should be pointed that the intramolecular energy transfer efficiency in dendrimer system is much higher than that of an intermolecular energy transfer in the simple mixture of the core and the peripherals. The obvious fluorescence quenching of the donor CZ in dendrimers is shown in Figure 7. This conclusion is further supported by the dependence of the fluorescence on the solution concentrations. The fluorescence of the simple mixture is much more significantly dependent on the concentration than that for the corresponding dendrimers. Indeed, for a diluted mixture almost no fluorescent quenching of the CZ chromophore was observed, which indicates the less effective intermolecular energy transfer process in the mixture.

Photoinduced electron transfer between the core and peripheral units might also take place, which should be further studied by transient fluorescence spectra. The reference compound carbazole exhibits only a single-exponential decay with a fluorescent lifetime of 8.401 ns (Figure 8). In contrast, the carbazole units CZ in dendrimers 4CZ-NP3 and 8CZ-NP3 have dual-exponential decay characteristics (Figure 8). That is, for 4CZ-NP3, the CZ unit has two components with fluorescent lifetimes of 0.314 ns (53.86%) and 7.713 ns (46.14%). 8CZ-NP3 shows two character fluorescent lifetimes for the CZ unit with 0.533 ns (22.55%) and 7.818 ns (77.45%). The relatively short-lived fluorescent lifetimes can be assignable to the residual component after the photochemical communication between CZ units and naphthalimide cores. Comparing the shorter lifetime components of the second-generation dendrimer 4CZ-NP3 (0.314 ns) and the third-generation dendrimer 8CZ-NP3 (0.553 ns), the fluorescence of the CZ unit in 4CZ-NP3 is more obviously quenched due to the effective intramolecular energy transfer and the photoinduced electron transfer to the core. From the semiempirical simulation of hyperchemistry, the average rate constant ($k = 1/\tau_D(R_0/R_1)^6$) for the fluorescence decay became smaller as the CZ units increased from 4CZ-NP3 (2.42 ns^{-1}) to 8CZ-NP3 (1.3 ns^{-1}), which is almost consistent with the core luminescence-enhancing ratio for each donor contribution.

Table 2. Fluorescence Lifetimes of 4CZ-NP3 (λ_{em} = 350 nm) Obtained from the Transient Decay against the Concentration Variation of TiO_2 Excited at the Absorption Peak of the CZ (330 nm)

compound (concn (mol·L^{-1}))	lifetime τ (ns) (component ratio (%))	
4CZ-NP3 (1.0 × 10^{-5})	0.31 (53.86)	7.71 (46.14)
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.0 × 10^{-5})	0.69 (73.00)	8.22 (27.00)
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (3.0 × 10^{-5})	0.60 (100)	
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (6.0 × 10^{-5})	0.59 (100)	
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (9.0 × 10^{-5})	0.73 (100)	
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.2 × 10^{-4})	0.54 (100)	
4CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.5 × 10^{-4})	0.59 (100)	

Table 3. Fluorescence Lifetime of 8CZ-NP3 (λ_{em} = 350 nm) Obtained from the Transient Decay against the Concentration Variation of TiO_2 Excited at the Absorption Peak of the CZ (330 nm)

compound (concn (mol·L^{-1}))	lifetime τ (ns) (component ratio (%))	
8CZ-NP3 (1.0 × 10^{-5})	0.53 (22.55)	7.82 (77.45)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.0 × 10^{-5})	1.03 (31.62)	7.89 (68.38)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (3.0 × 10^{-5})	1.31 (41.18)	7.51 (58.82)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (6.0 × 10^{-5})	1.49 (53.78)	8.29 (46.22)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (9.0 × 10^{-5})	1.22 (61.85)	8.35 (38.15)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.2 × 10^{-4})	1.68 (66.71)	9.38 (33.29)
8CZ-NP3 (1.0 × 10^{-5}) + TiO_2 (1.5 × 10^{-4})	1.12 (68.92)	8.19 (31.08)

It is well-known that TiO_2 nanoparticle can be utilized as a "trap" for photoinduced electrons. [21] When nanoparticle TiO_2 was added to the solution of 4CZ-NP3 and 8CZ-NP3 in THF, it can be expected that the interaction between the core NP and the peripheral CZ would be disturbed, thus monitoring the mechanism of light-harvesting in the dendrimers. In fact, with increasing concentration of TiO_2, the content percentage of the relatively short-lived component characterized for the CZ unit in 4CZ-NP3 and 8CZ-NP3 increased (Tables 2 and 3). In particular, when the concentration of TiO_2 reached 3 × 10^{-5} mol·L^{-1}, 4CZ-NP3 exhibits only single short-live component fluorescence at 350 nm, the long-live component is disappeared due to the electron trapping by nanoparticle TiO_2. This indicates an efficient electron transfer between TiO_2 nanoparticles and the CZ units of the dendrimers. In this case the intramolecular interaction between the core NP and the peripheral CZ units is efficiently inhibited. The interaction between the peripheral CZ units and TiO_2 is dominated, which decreases the light-antenna effect

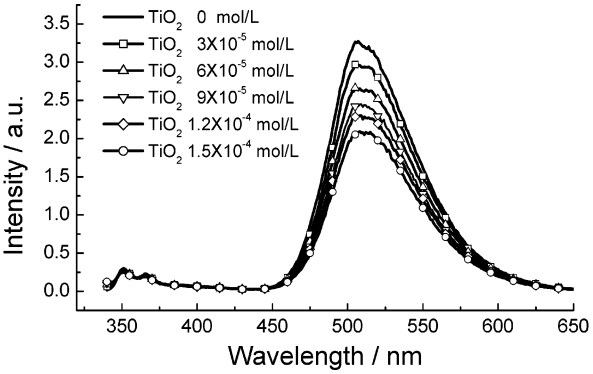


Figure 9. Emission spectra of 4CZ-NP3 in THF (1×10^{-5} mol·L^{-1}) plotted against different concentrations of TiO_2 excited at the absorption peak of carbazole (330 nm).

Table 4. Oxidation Potentials and Calculated HOMO and LUMO Energies for the Dendrimers[a]

compounds	E_{ox} (V vs reference electrode Ag/AgCl)	HOMO (eV)	LUMO (eV)
2OXZ-NP1	1.24	−5.52	−3.04
4OXZ-NP1	1.24	−5.52	−3.04
2OXZ-NP2	1.34	−5.62	−3.01
4OXZ-NP2	1.34	−5.62	−3.01
2OXZ-NP3	1.39	−5.67	−2.97
4OXZ-NP3	1.39	−5.67	−2.97
2CZ-NP1	0.90	−5.18	−3.04
4CZ-NP1	0.93	−5.21	−3.04
8CZ-NP1	0.93	−5.21	−3.04
2CZ-NP2	0.93	−5.21	−3.01
4CZ-NP2	0.93	−5.21	−3.01
8CZ-NP2	0.93	−5.21	−3.01
2CZ-NP3	0.93	−5.21	−2.97
4CZ-NP3	0.93	−5.21	−2.97
8CZ-NP3	0.93	−5.21	−2.97

[a] The oxidative potential of reference ferrocene (Fc) vs reference electrode Ag/AgCl is 0.52 V.

between the CZ units and the core naphthalimide chromophore, as shown in Figure 9.

Electrochemical Properties. Cyclic voltammetry measurements were carried out at a platinum electrode using millimolar solutions in CH_2Cl_2 containing 0.1 M of the support electrolyte, tetrabutylammonium perchloride, in a three-electrode cell and potentiostat assembly. For the dendrimers with carbazole peripheral groups, the oxidative sweep is predominated by two reversible peaks originated from the carbazole unit appeared at 0.93 and 1.24 V (shown in Figure 10), with which an irreversible peak of the naphthalimide unit located between 1.10 and 1.30 V is overlapped. While for the dendrimers with oxadiazole peripheral groups, only an irreversible peak in oxidative scan arises from the naphthalimide unit. The HOMO energy values for the dendrimers were calculated according to the value of −4.8 eV for ferrocene (Fc) with respect to zero vacuum level. And the optical edge was utilized to derive the band gap and give the LUMO energy values for the dendrimers.[22] The measured oxidation potentials (vs reference electrode Ag/AgCl) and HOMO and LUMO energy values for dendrimers are summarized in Table 4. It should be noted that the shell effect does not distinctly occur, such as redox wave broadening or shift,[23] which can be attributed to the fact that the dendrimers synthesized in this work are not global shape.

Thermal Stability. Starburst compounds and dendrimers are capable of preventing spatial reorientation of the molecules, thus eliminating the recrystallization tendency and favoring the formation of a stable amorphous state. This molecular design strategy had been successfully applied to develop triarylamine-based hole-transporting materials.[24] For the dendrimers in this study, the second-generation dendrimers have a higher melting point than those of the first- and third-generation dendrimers (Table 1). For instance, careful examination of DSC thermograms for 4CZ-NP3 revealed that

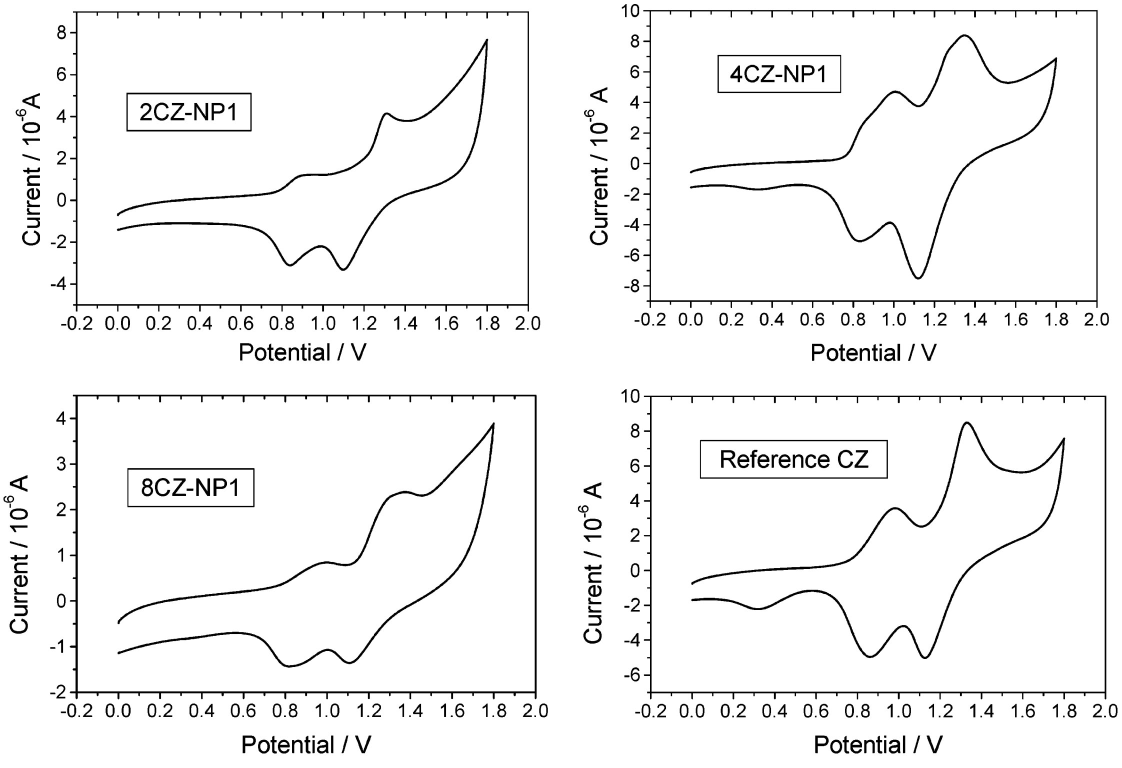


Figure 10. Cyclic voltammogram in CH_2Cl_2: (a) 2CZ-NP1, (b) 4CZ-NP1, (c) 8CZ-NP1, and (d) reference carbazole.

Table 5. EL Device Performances of 2CZ-NP3 and 8CZ-NP3

EL device structure	bias (V)	current (mA)	luminance (cd/m^2)	eff (%)	EL peak (λ_{max}/nm)
ITO//PEDOT(65 nm)//2CZ-NP3(120 nm)//Ba (4 nm) /Al (150 nm)	12.48	7.73	308	0.50	526
	11.7	5.01	190	0.48	
ITO//PEDOT(65 nm)//8CZ-NP3(80 nm)//Ba (4 nm) /Al (150 nm)	15.30	41.94	59	0.02	526
	3.12	5.35	5	0.01	

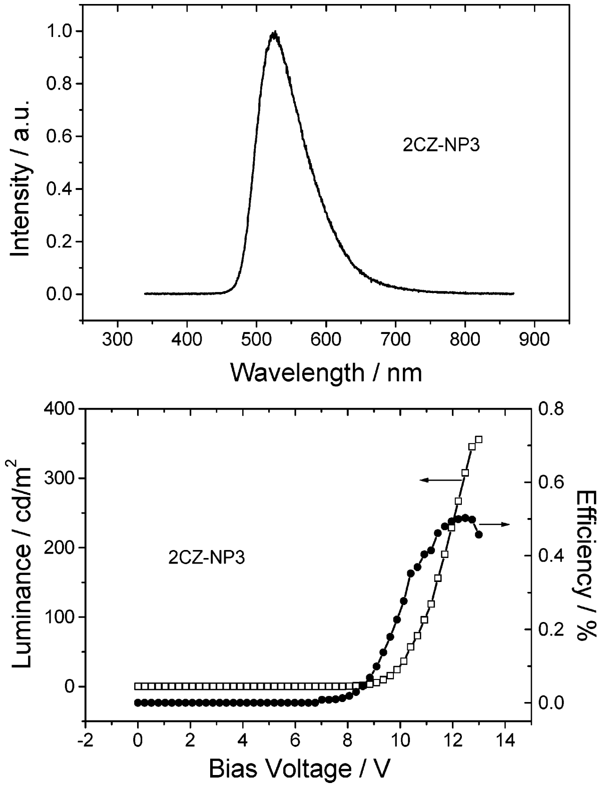


Figure 11. EL spectrum and luminance−efficiency−voltage characteristics of the device ITO//PEDOT(65 nm)//2CZ-NP3-(120 nm)//Ba (4 nm)/Al (150 nm).

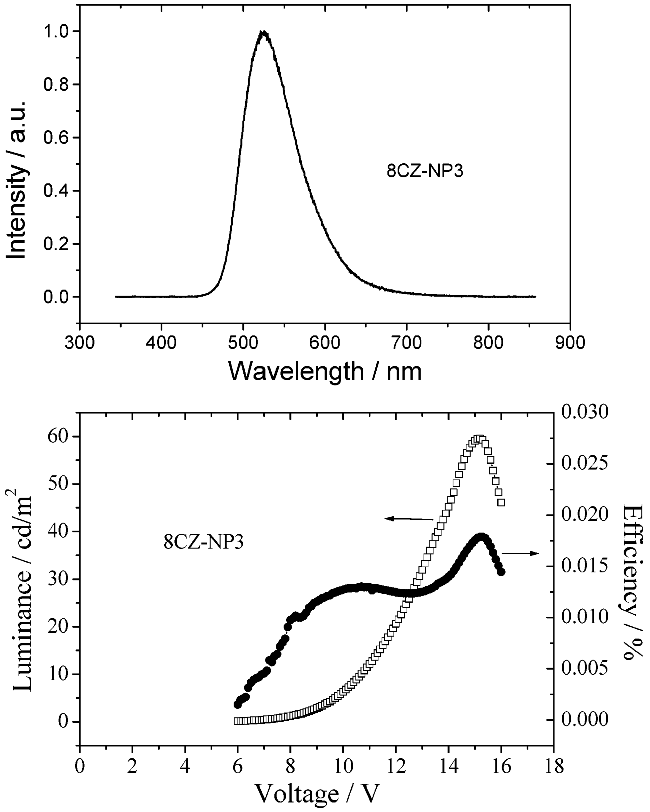


Figure 12. EL spectrum and luminance−efficiency−voltage characteristics of device and ITO//PEDOT(65 nm)//8CZ-NP3 (80 nm)//Ba (4 nm)/Al (150 nm).

there is no distinct glass transition state below 180 °C (shown in Figure S-1 of the Supporting Information). When the sample was cooled under rate of 10 °C /min from 180 to 50 °C, no distinct crystallization phase was observed. The glass transition temperatures (T_g) of 2OXZ-NP3 and 4OXZ-NP2 are located at 139 and 102 °C, respectively. No distinct glass transition state was observed for them when taken on the second heating. Thus, thermal analysis results indicate that such dendron-functionalized luminescent materials have good thermal stability, which is very essential for fabricating stable organic EL devices.

Electroluminescent Properties. The main objective of this study is to develop novel dendron-functionalized luminescent materials. For the preliminary studies in light-emitting devices, a dendrimer acting as an active single-layer luminescent material was utilized (ITO//PEDOT(65 nm)//dendrimers//Ba (4 nm)/Al (150 nm)). Preliminary results of EL devices made with these dendrimers are listed in Table 5. In both EL devices, only the emission peak at 526 nm was detected (Figures 11 and 12). Compared with the PL spectrum of the dendrimers in solid film, the EL spectra are similar to the PL spectra of corresponding dendrimers, which indicates the same band gap involved in the EL and the PL spectra. The peripheral of carbazole unit did not emit light in the operation of the devices. It is believed that the carbazole unit decreases the HOMO orbital energy by 0.4 eV (Table 5), which reduces the hole-injecting barrier and thus facilitates the hole injection from ITO electrode. Electrons are injected from the cathode to the LUMO orbital of the naphthalimide moiety with high electron affinity (about 3.0 eV) and holes are also injected from ITO (4.6 eV) to the HOMO orbital of the carbazole moiety (5.2 eV). Then the holes are transferred to HOMO orbital of the naphthalimide (ca. 5.5 eV). Hence, the holes and electrons are trapped in the naphthalimide moiety to form exciton that undergoes radiative decay resulting in the naphthalimide characteristic emission.

Conclusions

We have synthesized three generations of a novel series of dendrimers that contain naphthalimide cores, Fréchet-type poly(aryl ether) dendrons, and functional peripheral groups such as carbazole or oxadiazole units to improve the charge carrier-transporting property for the application in OLEDs. This modular construction enables the processing and electronic properties to be tuned independently. This is a significant advantage over polymeric or molecular materials where attempts to tune the solubility often lead to an undesirable change in the emission properties. We have demonstrated the fact that the peripheral chromophores CZ or OXZ have specific light-antenna and enhanced core luminescence properties, whose efficiency is dependent on the dendrimer generation number. Time-resolved luminescence further supported the conclusion that the contribution tendency for each peripheral donor is decreased with increasing the generation number, especially for the third-generation dendrimers. Specifically, the intensity of an enhanced emission for the dendrimers synthesized in this study is stronger than that of a direct-core emission; that is, the light harvest for the luminescence of the chromophore by the light antenna is more efficient than direct excitation at the absorption maximum by an external light source. All dendrimers including three generations can be spin-coated from solution to form good quality thin films and have good thermal stability. The preliminary EL results with a single-layer architecture made with the dendrimers demonstrate that these dendrimers could be utilized as a promising active nondoping emitter with charge carrier-transporting ability.

Experimental Section

Instrumentation. Melting points were measured on an X4 micromelting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer. MS were recorded on FAB or MALDI−TOF mass spectroscopy using α-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. The nanoparticle TiO_2 used in this study is produced by Alfa Aesar Co. and is the anatase 99.9% (metals basis), which is for research and development use only, with reagent number 27 AF-39953.

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

The dendrimer films were spin-coated on ITO glass from the chlorobenzene solution. 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-ehtylenedioxythiophene-poly-styrenesulfonic acid) (PEDOT) (Bayer AG). The active dendrimer layer was spin-coated from 2 wt % chlorobenzene solution. The cathode layer of Ba (4 nm)/Al (150 nm) was thermally evaporated in a vacuum chamber (pressure $< 2 \times 10^{-4}$ Pa). The thickness of different layers was measured by Tencor α-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 with a hydrogen-filled flash lamp/or a nitrogen lamp as the excitation source. Data were analyzed using a nonlinear least-squares fitting program, with deconvolution of the exciting pulse being ~200 ps.

Synthesis. (CZ)$_2$-(G-1)-OH (4) ([3,5-Bis(4-carbazol-9-yl-butyloxy)phenyl]methanol). A mixture of 9-(4-bromo-butyl)-9*H*-carbazole (4.4 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), potassium carbonate (3.4 g, 60 mmol), and 18-crown-6 (0.38 g, 1.42 mmol) in anhydrous acetone (50 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water, and the aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **4** as pale yellow powder (3.44 g, yield 82.8%). Mp: 118−120 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.8$ (m, 4 H, $-CH_2$), 2.1 (m, 4 H, $-CH_2$), 3.85 (t, $J = 6.1$ Hz, 4 H, $-NCH_2-$), 4.37 (t, $J = 7.1$ Hz, 4 H, $-OCH_2-$), 4.7 (s, $-C\boldsymbol{H}_2OH$, 2 H), 6.25 (s, 1 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.2 (t × d, $J = 6.8$ Hz, $J = 1.0$ Hz, 4 H, Ph−H(CZ)), 7.4 (d, $J = 8.0$ Hz, 4 H, Ph−H(CZ)), 7.48 (t × d, $J = 7.9$ Hz, $J = 1.0$ Hz, 4 H, Ph−H(CZ)), 8.2 (d, $J = 7.8$ Hz, 4 H, Ph−H(CZ)).

(CZ)$_2$-(G-1)-OSO$_2$Me (5) (Methanesulfonic Acid 3,5-Bis-(4-carbazol-9-yl-butyloxy)benzyl Ester). A solution of compound **4** (3.1 g, 1.43 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature. $MeSO_2Cl$ (0.162 g, 1.43 mmol) and triethylamine (0.144 g, 1.43 mmol) were added dropwise to the solution and stirred for 24 h. Then water was added to the solution. The aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The extract was dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography eluting on silica gel with CH_2Cl_2 to give a white powder (1.01 g, yield 94%). Mp: 148−149 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.8$ (m, 4 H, $-CH_2$), 1.6 (s, 3 H, $-CH_3$), 2.1 (m, 4 H, $-CH_2$), 3.85 (t, 4 H, $J = 6.0$ Hz, $-NCH_2-$), 4.37 (t, $J = 7.1$ Hz, 4 H, $-OCH_2-$), 4.5 (s, 2 H, $-C\boldsymbol{H_2}OSO_2Me$), 6.30 (s, 1 H, Ph−H), 6.45 (s, 2 H, Ph−H), 7.2 (t, 4 H, Ph−H(CZ), $J = 7.3$ Hz), 7.4 (d, 4 H, Ph−H(CZ), $J = 8.0$ Hz), 7.48 (t × d, 4 H, Ph−H(CZ), $J = 7.8$ Hz, $J = 1.0$ Hz), 8.2 (d, 4 H, Ph−H(CZ), $J = 8$ Hz).

(OXZ)$_2$-(G-1)-OH (6) ((3,5-Bis-{4-[5-(4-*tert*-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]benzyloxy}phenyl)methanol). A mixture of 2-(4-bromomethyl-phenyl)-5-(4-*tert*-butyl-phenyl)-[1,3,4]oxadiazole (OXZ-Br, 5.4 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), potassium carbonate (3.4 g, 60 mmol), and 18-crown-6 (0.38 g, 1.42 mmol) in anhydrous acetone (50 mL) was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water, and the aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **6** as a pale yellow crystalline solid (4.2 g, yield 82.4%). Mp: 106−108 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.3$ (s, 18 H, $-CH_3$), 4.7 (s, 2 H, $-C\boldsymbol{H}_2OH$), 5.2 (s, 4 H, $-CH_2-$), 6.5 (s, 1 H, Ph−H), 6.7 (s, 2 H, Ph−H), 7.5 (d, 4 H, $J = 8.1$ Hz), 7.55 (d, 4 H, $J = 7.8$ Hz), 8.05 (d, 4 H, $J = 8.0$ Hz), 8.15 (d, 4 H, $J = 7.8$ Hz).

(OXZ)$_2$-(G-1)-OSO$_2$Me (7) (Methanesulfonic Acid 3,5-Bis{4-[5-(4-*tert*-butylphenyl)-[1,3,4]oxadiazol-2-yl]benzyloxy}benzyl Ester). A solution of compound **6** (6.1 g, 1.25 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature. $MeSO_2Cl$ (0.142 g, 1.25 mmol) and triethylamine (0.126 g, 1.25 mmol) were added dropwise to the solution and stirred for 24 h. Then water was added to the solution. The aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The extract was dried with anhydrous $MgSO_4$ and evaporated to give compound 7 (4.2 g, yield 95.5%). Mp: 104−105 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.3$ (s, 18 H, $-CH_3$), 1.6 (s, 3 H, $-CH_3$), 4.5 (s, 2 H, $-CH_2O-$), 5.2 (s, 4 H, $-CH_2-$), 6.5 (s, 1 H, Ph−H), 6.7 (s, 2 H, Ph−H), 7.5 (d, 4 H, $J = 8.4$ Hz), 7.55 (d, 4 H, $J = 7.6$ Hz), 8.05 (d, 4 H, $J = 8.0$ Hz), 8.15 (d, 4 H, $J = 8.3$ Hz).

(CZ)$_2$-(G-1)-Br. A mixture of compound **4** (1.0 g, 1.72 mmol) and CBr_4 (0.44 g, 1.25 mmol) in dry CH_2Cl_2 (20 mL) was cooled to 0 °C. Triphenylphosphine (0.4 g, 1.5 mmol) was then slowly added and stirred for 5 h. After CH_2Cl_2 was removed, the product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to give a pale yellow powder (1.02 g, yield 92.1%). Mp: 163−164 °C. ^1H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.8$ (m, 4 H, $-CH_2$), 2.1 (m, 4 H, $-CH_2$), 3.85 (t, 4 H, $J = 6.1$ Hz, $-NCH_2-$), 4.2 (s, 2 H, $-CH_2Br$), 4.37 (t, $J = 7.1$ Hz, 4 H, $-OCH_2-$), 6.30 (s, 1 H, Ph−H), 6.45 (s, 2 H, Ph−

H), 7.2 (t, 4 H, Ph−H(CZ), J = 7.3 Hz), 7.4 (d, 4 H, Ph−H(CZ), J = 8.0 Hz), 7.48 (t × d, 4 H, Ph−H(CZ), J = 7.8 Hz, J = 1.0 Hz), 8.2 (d, 4 H, Ph−H(CZ), J = 7.8 Hz).

$(CZ)_4$-(G-2)-OH (1). A mixture of $(CZ)_2$-(G-1)-Br (8.3 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), potassium carbonate (3.4 g, 60 mmol), and 18-crown-6 (0.38 g, 1.42 mmol) in 50 mL of anhydrous THF was heated at reflux and stirred vigorously under nitrogen for 56 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water, and the aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The combined extracts were dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give 1 as pale yellow powder (7.1 g, yield 79.2%). Mp: 96−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.8 (m, 8 H, $-CH_2$), 2.05 (m, 8 H, $-CH_2$), 3.85 (t, J = 6.1 Hz, 8 H, $-NCH_2-$), 4.37 (t, J = 7.0 Hz, 8 H, $-OCH_2-$), 4.6 (s, $-C\boldsymbol{H}_2OH$, 2 H,), 4.9 (4 H, $-OCH_2-$), 6.25 (s, 2 H, Ph−H), 6.4 (s, 5 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.2 (t × d, J = 7.8 Hz, J = 1.0 Hz, 8 H, Ph−H(CZ)), 7.4 (d, J = 7.9 Hz, 8 H, Ph−H(CZ)), 7.48 (t × d, J = 7.9 Hz, J = 1.0 Hz, 8 H, Ph−H(CZ)), 8.2 (d, J = 7.7 Hz, 8 H, Ph−H(CZ)).

$(CZ)_4$-(G-2)-OSO_2Me (2). A solution of $(CZ)_4$-(G-2)-OH (1.8 g, 1.43 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature. $MeSO_2Cl$ (0.162 g, 1.43 mmol) and triethylamine (0.144 g, 1.43 mmol) were added dropwise to the solution and stirred for 24 h. Then water was added to the solution. The aqueous layer was extracted with CH_2Cl_2 (40 mL × 3). The extract was dried with anhydrous $MgSO_4$ and evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give white powder (1.8 g, yield 94.6%). Mp: 70−71 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.6 (s, 3 H, $-CH_3$), 1.8 (m, 8 H, $-CH_2$), 2.05 (m, 8 H, $-CH_2$), 3.85 (t, J = 6.1 Hz, 8 H, $-NCH_2-$), 4.37 (t, J = 7.0 Hz, 8 H, $-OCH_2-$), 4.5 (s, $-C\boldsymbol{H}_2OMS$, 2 H), 4.9 (s, 4 H, $-OCH_2-$), 6.25 (s, 2 H, Ph−H), 6.4 (s, 5 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.2 (*t*, 8 H, Ph−H(CZ)), 7.4 (d, 8 H, Ph−H(CZ)), 7.48 (t, 8 H, Ph−H(CZ)), 8.1 (d, J = 7.6 Hz, 8 H, Ph−H(CZ)).

2OXZ-NP1. A mixture of compound **7** (0.45 g, 0.56 mmol), compound **11** (0.10 g, 0.28 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 2OXZ-NP1 (0.16 g, yield 54%). Mp: 149−150 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.35 (s, 18 H, $-CH_3$), 3.15 (s, 6 H, $N(CH_3)_2$), 5.15 (s, 4 H, PhO−CH_2−Ph), 5.38 (s, 2 H, PhCOO−CH_2−Ph), 6.6 (s, 1 H, Ph−H), 6.75 (s, 2 H, Ph−H), 7.15 (d, 1 H, naphthalene-H, J = 8.3 Hz), 7.4 (d, 2 H, Ph−H, J = 7.2 Hz), 7.55 (d, 4 H, Ph−H(OXZ, J = 8.1 Hz), 7.6 (d, 4 H, Ph−H(OXZ), J = 8.2 Hz), 7.7 (t, 1 H, naphthalene-H), 8.05 (d, 4 H, Ph−H(OXZ), J = 8.5 Hz), 8.18 (d, 4 H, Ph−H(OXZ), J = 8.1 Hz), 8.25 (d, 2 H, Ph−H), 8.49 (d, 1 H, naphthalene-H), 8.51 (d, 1 H, naphthalene-H), 8.6 (d, 1 H, naphthalene-H, J = 7.2 Hz).

2OXZ-NP2. A mixture of compound **7** (0.40 g, 0.5 mmol), compound **12** (0.10 g, 0.25 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was then filtered and purified by column chromatography on silica gel. eluting with CH_2Cl_2 to give 2OXZ-NP2 (0.103 g, yield 51%). Mp: 154−155 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.3 (s, 18 H, $-CH_3$), 1.75 (m, 2 H, $-CH_2-$), 1.9 (m, 4 H, $-CH_2-$), 3.5 (t, 4 H, N−CH_2), 5.2 (s, 4 H, PhO−CH_2−Ph), 5.4 (s, 2 H, PhCOO−CH_2−Ph), 6.6 (s, 1 H, Ph−H), 6.75 (s, 2 H, Ph−H), 7.2 (d, 1 H, naphthalene-H, J = 8.1 Hz), 7.4 (d, 2 H, Ph−H), 7.6 (d, 4 H, Ph−H(OXZ)), 7.65 (d, 4 H, Ph−H(OXZ)), 7.72 (t, 1 H, naphthalene-H), 8.1 (d, 4 H, Ph−H(OXZ), J = 7.9 Hz), 8.2 (d, 4 H, Ph−H(OXZ), J = 7.8 Hz), 8.25 (d, 2 H, Ph−H, J = 8.4 Hz), 8.4 (d, 1 H, naphthalene-H, J = 8.5 Hz), 8.5 (d, 1 H, naphthalene-H, J = 8.1 Hz), 8.6 (d, 1 H, naphthalene-H, J = 7.2 Hz).

2OXZ-NP3. A mixture of compound **7** (0.4 g, 0.5 mmol), compound **13** (0.1 g, 0.25 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 2OXZ-NP3 (0.141 g, yield 51%). Mp: 154−155 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.3 (s, 18 H, $-CH_3$), 3.3 (t, 4 H, N−CH_2, J = 4.4 Hz), 4.05 (t, 4 H, O−CH_2, J = 4.4 Hz), 5.2 (s, 4 H, PhO−CH_2−Ph), 5.4 (s, 2 H, PhCOO−CH_2−Ph), 6.6 (s, 1 H, Ph−H), 6.75 (s, 2 H, Ph−H), 7.2 (d, 1 H, naphthalene-H, J = 8.1 Hz), 7.4 (d, 2 H, Ph−H), 7.6 (d, 4 H, Ph−H(OXZ)), 7.65 (d, 4 H, Ph−H(OXZ)), 7.72 (t, 1 H, naphthalene-H), 8.1 (d, 4 H, Ph−H(OXZ), J = 7.9 Hz), 8.2 (d, 4 H, Ph−H(OXZ), J = 7.8 Hz), 8.25 (s, 2 H, Ph−H), 8.4 (d, 1 H, naphthalene-H, J = 8.5 Hz), 8.5 (d, 1 H, naphthalene-H, J = 8.1 Hz), 8.6 (d, 1 H, naphthalene-H, J = 7.2 Hz).

4OXZ-NP1. A mixture of compound **7** (0.41 g, 0.52 mmol), compound **9** (0.1 g, 0.25 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 4OXZ-NP1 (0.073 g, yield 16.3%). Mp: 196−198 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 1.3 (s, 36 H, $-CH_3$), 3.1 (s, 6 H, $-N(CH_3)_2$), 5.1 (s, 8 H, PhO−CH_2−Ph), 5.4 (s, 4 H, PhCOO−CH_2−Ph), 6.5 (s, 2 H, Ph−H), 6.7 (s, 4 H, Ph−H), 7.15 (d, J = 8.3 Hz, 1 H, naphthalene-H), 7.5 (d, J = 8.3 Hz, 8 H, Ph−H(OXZ)), 7.6 (d, J = 8.0 Hz, 8 H, Ph−H (OXZ)), 7.7 (t, J = 7.9 Hz, 1 H, naphthalene-H), 8.05 (d, J = 8.2 Hz, 8 H, Ph−H(OXZ)), 8.13 (d, J = 8.1 Hz, 8 H, Ph−H(OXZ)), 8.25 (s, 2 H, Ph−H), 8.44 (d, J = 8.2 Hz, 1 H, naphthalene-H), 8.48 (d, J = 8.2 Hz, 1 H, naphthalene-H), 8.6 (d, J = 7.1 Hz, 1 H, naphthalene-H), 8.9 (s, 1 H, Ph−H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.121, 35.096, 44.739, 66.941, 69.443, 82.711, 107.354, 112.367, 121.049, 123.552, 126.047, 126.779, 127.122, 127.778, 138.223, 140.550, 155.351, 159.830, 164.118, 164.675, 171.648. MS (FAB): *m*/*z* [M^+] 1811, [M^+ + Na] 1833.

4OXZ-NP2. A mixture of compound **7** (0.38 g, 0.473 mmol), compound **10** (0.10 g, 0.23 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 4OXZ-NP2 (0.103 g, yield 24.8%). Mp: 172−173 °C.^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.4 (s, 36 H, $-CH_3$), 1.65 (m, 2 H, $-CH_2-$), 1.85 (m, 4 H, $-CH_2-$), 3.2 (t, 4 H, $-NCH_2$), 5.1 (s, 8 H, PhO−CH_2−Ph), 5.4 (s, 4 H, PhCOO−CH_2−Ph), 6.5 (s, 2 H, Ph−H), 6.7 (s, 4 H, Ph−H), 7.25 (d, J = 8.2 Hz, 1 H, naphthalene-H), 7.55 (d, J = 8.0 Hz, 8 H, Ph−H(OXZ)), 7.6 (d, J = 7.8 Hz, 8 H, Ph−H(OXZ)), 7.7 (t, J = 7.9 Hz, 1 H, naphthalene-H), 8.05 (d, J = 8.0 Hz, 8 H, Ph−H(OXZ)), 8.13 (d, J = 7.8 Hz, 8 H, Ph−H(OXZ)), 8.25 (s, 2 H, Ph−H), 8.44 (d, J = 8.5 Hz, 1 H, naphthalene-H), 8.48 (d, J = 8.0 Hz, 1 H, naphthalene-H), 8.6 (d, J = 7.2 Hz, 1 H, naphthalene-H), 8.9 (s, 1 H, Ph−H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.392, 31.121, 35.088, 69.436, 107.354, 121.065, 126.047, 126.779, 127.130, 127.786, 137.613, 140.543, 155.344, 159.838, 164.705, 168.314, 198.664, 212.733, 230.181. MS (FAB): *m*/*z* [M^+] 1852.

4OXZ-NP3. A mixture of compound **7** (0.38 g, 0.473 mmol), compound **3** (0.10 g, 0.22 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel eluting with CH_2Cl_2 to give 4OXZ-NP3 (0.086 g, yield 20.7%). Mp: 195−196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.4 (s, 36 H, $-CH_3$), 3.3 (t, 4 H, $-NCH_2-$), 4.0 (t, 4 H, $-OCH_2-$), 5.1 (s, 8 H, PhO−CH_2−Ph), 5.4 (s, 4 H, PhCOO−CH_2−Ph), 6.5 (s, 2 H, Ph−H), 6.7 (s, 4 H, Ph−H), 7.25 (d, J = 8.1 Hz, 1 H, naphthalene −H), 7.55 (d, J = 8.0 Hz, 8 H, Ph−H(OXZ)), 7.6 (d, J = 7.8 Hz, 8 H, Ph−H(OXZ)), 7.7 (t, J = 7.6 Hz, 1 H, naphthalene-H), 8.05 (d, J = 7.9 Hz, 8 H, Ph−H(OXZ)), 8.13 (d, J = 7.7 Hz, 8 H, Ph−H(OXZ)), 8.25 (s, 2 H, Ph−H), 8.44 (d, J = 8.3 Hz, 1 H, naphthalene-H), 8.48 (d, J = 7.8 Hz, 1 H), naphthalene-H), 8.6 (d, $J = 6.9$ Hz, 1 H, naphthalene-H), 8.9 (s, 1 H, Ph−H).

2CZ-NP1. A mixture of compound **5** (0.33 g, 0.52 mmol), compound **11** (0.1 g, 0.28 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 2CZ-NP1 (0.21 g, yield 55.3%). Mp: 136−137 °C.^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.8$ (m, 4 H, $-CH_2-$), 2.1 (m, 4 H, $-CH_2$), 3.05 (s, 6 H, $-N(CH_3)_2$), 3.85 (t, $J = 6.1$ Hz, 4 H, $-NCH_2-$), 4.37 (t, $J = 6.5$ Hz, 4 H, $-CH_2O-$), 5.25 (s, 2 H, $-CH_2O-$), 6.3 (s, 1 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.2 (d, $J = 8.3$ Hz, 1 H, naphthalene-H), 7.25 (t, $J = 7.1$ Hz, 4 H, Ph−H(CZ)), 7.38 (d, $J = 7.9$ Hz, 4 H, Ph−H (CZ)), 7.42 (t, $J = 7.4$ Hz, 4 H, Ph−H(CZ)), 7.5 (d, $J = 7.1$ Hz, 2 H, Ph−H), 7.75 (t, $J = 7.8$ Hz, 1 H, naphthalene-H), 8.05 (d, $J = 7.9$ Hz, 4 H, Ph−H(CZ)), 8.25 (d, $J = 8.4$ Hz, 2 H, Ph−H), 8.5 (d, $J = 8.5$ Hz, 1 H, naphthalene-H), 8.6 (d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.75 (d, $J = 7.2$ Hz, 1 H, naphthalene-H).

2CZ-NP2. A mixture of compound **5** (0.304 g, 0.473 mmol), compound **12** (0.1 g, 0.25 mmol), and potassium carbonate-(0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 2CZ-NP2 (0.18 g, yield 50%). Mp: 136−138 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.65$ (m, 2 H, $-CH_2-$), 1.75 (m, 4 H, $-CH_2$), 1.8 (m, 4 H, $-CH_2$), 2.1 (m, 4 H, $-CH_2$), 3.2 (t, 4 H, $-NCH_2$), 3.85 (t, $J = 6.1$ Hz, 4 H, $-NCH_2-$), 4.37 (t, $J = 7.1$ Hz, 4 H, $-CH_2-O$), 5.2 (s, 2 H, $-CH_2O-$), 6.3 (s, 1 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.2 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 7.2 (t, $J = 7.3$ Hz, 4 H, Ph−H(CZ)), 7.4 (d, $J = 8.0$ Hz, 4 H, Ph−H(CZ)), 7.45 (t, $J = 7.6$ Hz, 4 H, Ph−H(CZ)), 7.5 (d, $J = 8.0$ Hz, 2 H, Ph−H), 7.75 (t, $J = 7.9$ Hz, 1 H, naphthalene-H), 8.1 (d, $J = 7.9$ Hz, 4 H, Ph−H(CZ)), 8.25 (d, $J = 8.4$ Hz, 2 H, Ph−H), 8.5 (d, $J = 7.8$ Hz, 1 H, naphthalene-H), 8.6(d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.75 (d, $J = 7.2$ Hz, 1 H, naphthalene-H).

2CZ-NP3. A mixture of compound **5** (0.31 g, 0.473 mmol), compound **13** (0.1 g, 0.25 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 2CZ-NP3 (0.21, yield 58.3%). Mp: 150−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.8$ (m, 4 H, $-CH_2-$), 2.1 (m, 4 H, $-CH_2$), 3.27 (t, 4 H, $-NCH_2$), 3.9 (t, $J = 6.1$ Hz, 4 H, $N-CH_2$), 4.05 (t, $J = 4.3$ Hz, 4 H, $-CH_2-O$), 4.4 (t, $J = 7.0$ Hz, 4 H, $-CH_2O-$), 5.2 (s, 2 H, $-CH_2O-$), 6.3 (s, 1 H, Ph−H), 6.5 (s, 2 H, Ph−H), 7.19 (t, $J = 7.1$ Hz, 4 H, Ph−H(CZ)), 7.25 (d, $J = 8.3$ Hz, 1 H, naphthalene-H), 7.38 (d, $J = 7.9$ Hz, 4 H, Ph−H (CZ)), 7.42 (t, $J = 7.4$ Hz, 4 H, Ph−H(CZ)), 7.5 (d, $J = 7.1$ Hz, 2 H, Ph−H), 7.75 (t, $J = 7.8$ Hz, 1 H, naphthalene-H), 8.05 (d, $J = 7.9$ Hz, 4 H, Ph−H(CZ)), 8.25 (d, $J = 8.4$ Hz, 2 H, Ph−H), 8.5 (d, $J = 8.5$ Hz, 1 H, naphthalene-H), 8.6 (d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.75 (d, $J = 7.2$ Hz, 1 H, naphthalene-H).

4CZ-NP1. A mixture of compound **5** (0.33 g, 0.52 mmol), compound **9** (0.1 g, 0.25 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 4CZ-NP1 (0.063 g, yield 16.6%. Mp: 144−145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.8$ (m, 8 H, $-CH_2-$), 2.1 (m, 8 H, $-CH_2$), 3.05 (s, 6 H, $-N(CH_3)_2$), 3.85 (t, $J = 6.1$ Hz, 8 H, $-NCH_2-$), 4.37 (t, $J = 6.5$ Hz, 8 H, $-CH_2O-$), 5.25 (s, 4 H, $-CH_2O-$), 6.3 (s, 2 H, Ph−H), 6.5 (s, 4 H, Ph−H), 7.05 (d, $J = 8.3$ Hz, 1 H, naphthalene-H), 7.2 (t, $J = 7.1$ Hz, 8 H, Ph−H(CZ)), 7.38 (d, $J = 7.9$ Hz, 8 H, Ph−H (CZ)), 7.42 (t, $J = 7.4$ Hz, 8 H, Ph−H(CZ)), 7.6 (t, $J = 7.9$ Hz, 1 H, naphthalene-H), 8.05 (d, $J = 7.6$ Hz, 8 H, Ph−H(CZ)), 8.2 (s, 2 H, Ph−H), 8.37 (d, $J = 8.3$ Hz, 1 H, naphthalene-H), 8.42 (d, $J = 8.4$ Hz, 1 H, naphthalene-H), 8.5 (d, $J = 7.1$ Hz, 1 H, naphthalene-H), 8.82 (s, 1 H, Ph−H).

4CZ-NP2. A mixture of compound **5** (0.30 g, 0.473 mmol), compound **10** (0.10 g, 0.23 mmol), and potassium carbonate-(0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 4CZ-NP2 (0.072 g, yield 20.2%). Mp: 139−140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.65$ (m, 2 H, $-CH_2-$), 1.75 (m, 8 H, $-CH_2$), 1.8 (m, 4 H, $-CH_2$), 2.1 (m, 8 H, $-CH_2$), 3.2 (t, 4 H, $-NCH_2$), 3.85 (t, $J = 6.1$ Hz, 8 H, $-NCH_2-$), 4.37 (t, $J = 7.1$ Hz, 8 H, $-CH_2-O$), 5.2 (s, 4 H, $-CH_2O-$), 6.3 (s, 2 H, Ph−H), 6.5 (s, 4 H, Ph−H), 7.07 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 7.17 (t, $J = 7.3$ Hz, 8 H, Ph−H(CZ)), 7.38 (d, $J = 8.0$ Hz, 8 H, Ph−H(CZ)), 7.42 (t, $J = 7.6$ Hz, 8 H, Ph−H(CZ)), 7.6 (t, $J = 7.9$ Hz, 1 H, naphthalene-H), 8.1 (d, $J = 7.6$ Hz, 8 H, Ph−H(CZ)), 8.2 (s, 2 H, Ph−H), 8.37 (d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.42 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 8.5 (d, $J = 7.1$ Hz, 1 H, naphthalene-H), 8.82 (s, 1 H, Ph−H).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.831$, 25.788, 26.169, 26.866, 39.208, 42.656, 54.467, 67.132, 67.521, 69.741, 98.313, 101.365, 106.790, 108.621, 114.656, 115.144, 118.768, 120.294, 122.713, 122.796 125.612, 130.319, 131.326, 131.502, 131.845, 133.218, 134.752, 136.415, 137.712, 140.314, 160.150, 164.743. MS (FAB): m/z [M^+] 1574.

4CZ-NP3. A mixture of compound **5** (0.31 g, 0.473 mmol), compound **3** (0.10 g, 0.22 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 4CZ-NP3 (0.079 g, yield 22.3%). Mp: 194−195 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.7$ (m, 8 H, $-CH_2$), 1.95 (m, 8 H, $-CH_2$), 3.2 (t, $J = 4.0$ Hz, 4 H, $-NCH_2$), 3.8 (t, $J = 6.0$ Hz, 8 H, $N-CH_2$), 3.94 (t, $J = 4.2$ Hz, 4 H, $-CH_2-O$), 4.25 (t, $J = 2.1$ Hz, 8 H, $-CH_2O-$), 6.3 (s, 2 H, Ph−H), 6.4 (s, 4 H, Ph−H), 7.05 (d, $J = 8.1$ Hz, 1 H, naphthalene-H), 7.2 (t, $J = 7.3$ Hz, 8 H, Ph−H(CZ)), 7.3 (d, $J = 8.0$ Hz, 8 H, Ph−H(CZ)), 7.38 (t, $J = 7.5$ Hz, 8 H, Ph−H(CZ)), 7.55 (t, $J = 7.9$ Hz, 1 H, naphthalene-H), 7.98 (d, $J = 7.7$ Hz, 8 H, Ph−H(CZ)), 8.12 (s, 2 H, Ph−H), 8.33 (d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.37 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 8.45 (d, $J = 7.1$ Hz, 1 H, naphthalene-H), 8.82 (s, 1 H, Ph−H).^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 25.795$, 26.894, 42.672, 53.368, 66.911, 67.544, 106.813, 108.621, 109.758, 118.783, 120.309, 122.812, 125.619, 131.906, 137.712, 140.321, 160.166, 164.713. MS (FAB): m/z [M^+] 1576.

8CZ-NP1. A mixture of $(CZ)_4$-(G-2)-OMS (0.34 g, 0.25 mmol), compound **9** (0.05 g, 0.12 mmol), and potassium carbonate (0.1 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 8CZ-NP1 (0.095 g, yield 26.1%). Mp: 107−109 °C.^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.8$ (m, 16 H, $-CH_2-$), 2.1 (m, 16 H, $-CH_2$), 3.05 (s, 6 H, $-N(CH_3)_2$), 3.85 (t, 16 H, $-NCH_2-$), 4.3 (t, 16 H, $-CH_2O-$), 4.83 (s, 8 H, $-CH_2O-$), 5.25 (s, 4 H, $-CH_2O-$), 6.25 (s, 4 H, Ph−H), 6.45 (s, 8 H, Ph−H), 6.5 (s, 2 H, Ph−H), 6.7(s, 4 H, Ph−H), 7.15 (d, $J = 7.3$ Hz, 1 H, naphthalene-H), 7.2 (t, $J = 7.4$ Hz, 16 H, Ph−H(CZ)), 7.38 (d, $J = 8.0$ Hz, 16 H, Ph−H (CZ)), 7.42 (t, $J = 8.3$ Hz, 16 H, Ph−H(CZ)), 7.6(t, $J = 7.8$ Hz, 1 H, naphthalene-H), 8.1 (d, $J = 7.7$ Hz, 16 H, Ph−H(CZ)), 8.2 (s, 2 H, Ph−H), 8.37 (d, $J = 8.5$ Hz, 1 H, naphthalene-H), 8.42 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 8.5 (d, 1 H, naphthalene-H), 8.92 (s, 1 H, Ph−H). MS (MALDI−TOF): m/z [$M^+ + Na$] 2930.42, [$M^+ + K$] 2946.39.

8CZ-NP2. A mixture of $(CZ)_4$-(G-2)-OMS (0.31 g, 0.23 mmol), compound **10** (0.05 g, 0.11 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel, eluting with CH_2Cl_2 to give 8CZ-NP2 (0.1 g, yield 30%).

Mp: 115−117 °C.^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.65$ (m, 2 H, −CH$_2$−), 1.75 (m, 16 H, −CH$_2$−), 1.8 (m, 4 H, −CH$_2$), 2.0 (m, 16 H, −CH$_2$), 3.2 (t, 4 H, −NCH$_2$), 3.85 (t, 16 H, −NCH$_2$−), 4.37 (t, 16 H, −CH$_2$O−), 4.8 (s, 8 H, −CH$_2$O−), 5.25 (s, 4 H, −CH$_2$O−), 6.3 (s, 4 H, Ph−H), 6.45 (s, 8 H, Ph−H), 6.5 (s, 2 H, Ph−H), 6.65 (s, 4 H, Ph−H), 7.05 (d, $J = 8.3$ Hz, 1 H, naphthalene-H), 7.23 (t, $J = 7.2$ Hz, 16 H, Ph−H(CZ)), 7.38 (d, $J = 7.9$ Hz, 16 H, Ph−H (CZ)), 7.42 (t, $J = 7.4$ Hz, 16 H, Ph−H(CZ)), 7.62 (t, 1 H, naphthalene-H), 8.05 (d, $J = 7.6$ Hz, 16 H, Ph−H(CZ)), 8.18 (s, 2 H, Ph−H), 8.37 (d, 1 H, naphthalene-H), 8.42 (d, $J = 7.9$ Hz, 1 H, naphthalene-H), 8.48 (d, $J = 7.1$ Hz, 1 H, naphthalene-H), 8.9 (s, 1 H, Ph−H). MS (MALDI−TOF): m/z [M$^+$ + Na] 2970.40, [M$^+$ + K] 2986.33.

8CZ-NP3. A mixture of (CZ)$_4$-(G-2)-OMS (0.31 g, 0.23 mmol), compound **3** (0.05 g, 0.11 mmol), and potassium carbonate (0.10 g, 0.72 mmol) in dry DMF (10 mL) was heated to 100 °C and stirred vigorously for 24 h. After cooling to ambient temperature, the mixture was poured into water, filtered, and then purified by column chromatography on silica gel eluting with CH$_2$Cl$_2$ to give 8CZ-NP3 (0.11 g, yield 33%.) Mp: 116−118 °C.^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.75$ (m, 16 H, −CH$_2$−), 2.0 (m, 16 H, −CH$_2$), 3.1 (t, 4 H, −NCH$_2$), 3.85 (t, $J = 6.1$ Hz, 16 H, −NCH$_2$−), 3.9 (t, 4 H, −OCH$_2$), 4.3 (t, $J = 6.5$ Hz, 16 H, −CH$_2$O−), 4.8 (s, 8 H, −CH$_2$O−), 5.25 (s, 4 H, −CH$_2$O−), 6.25 (s, 4 H, Ph−H), 6.45 (s, 8 H, Ph−H), 6.5 (s, 2 H, Ph−H), 6.65 (s, 4 H, Ph−H), 6.95 (d, $J = 8.1$ Hz, 1 H, naphthalene-H), 7.2 (t, $J = 6.8$ Hz, 16 H, Ph−H(CZ)), 7.38 (d, $J = 7.8$ Hz, 16 H, Ph−H (CZ)), 7.42 (t, $J = 7.9$ Hz, 16 H, Ph−H(CZ)), 7.6(t, $J = 7.9$ Hz, 1 H, naphthalene-H), 8.05 (d, $J = 7.6$ Hz, 16 H, Ph−H(CZ)), 8.2 (s, 2 H, Ph−H), 8.37 (d, $J = 8.2$ Hz, 1 H, naphthalene-H), 8.42 (d, $J = 8.0$ Hz, 1 H, naphthalene-H), 8.45 (d, $J = 7.1$ Hz, 1 H, naphthalene-H), 8.9 (s, 1 H, Ph−H). MS (MALDI−TOF): m/z [M$^+$ + Na] 2972.46, [M$^+$ + K] 2988.39.

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Supporting Information Available: The concise scheme for the synthesis of the dendrimers, text giving experimental details for synthesizing intermediates **3**, **9**, **10**, **11**, **12**, and **13**, and a differential scanning calorimeter (DSC) trace of 4CZ-NP3 (Figure S-1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.

(3) (a) Furuta, P.; Brooks, J.; Thomopson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13165. (b) Beavington, R.; Frampton, M. J.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2003**, *13*, 211. (c) Wang, P. W.; Liu, Y. J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237. (d) Lo, S. C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater.* **2002**, *14*, 975. (e) Kwok, C. C.; Wong, M. S. *Macromolecules* **2001**, *34*, 6821; (f) Kwok, C. C.; Wong, M. S. *Chem. Mater.* **2002**, *14*, 3158.

(4) (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74. (b) Newkome, G. R.; He, E. F.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689. (c) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991.

(5) (a) Markham, J. P. J.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2646. (b) Anthopoulos, T. D.; Markham, J. P. J.; Namdas, E. B.; Lawrence, J. R.; Samuel, I. D. W.; Lo, S. C.; Burn, P. L. *Org. Electr.* **2003**, *4*, 71.

(6) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed.* **1990**, *29*, 138.

(7) Furuta, P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13173.

(8) Gilat, S. L.; Adronov, A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1422.

(9) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635.

(10) Kolosov, D.; Adamovich, V.; Djurovich, P.; Thompson, M. E.; Adachi, C. *J. Am. Chem. Soc.* 2002, *124*, 9945.

(11) Hasharoni, K.; Levanon, H.; Greenfield, S. R.; Gosztola, D. J.; Svec, W. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10228.

(12) (a) Poteau, X.; Brown, A. I.; Brown, R. G.; Holmes, C.; Matthew, D. *Dyes Pigments* **2000**, *47*, 91. (b) Gan, J. A.; Tian, H.; Wang, Z. H.; Chen, K. C.; Hill, J.; Lane, P. A.; Rahn, M. D.; Fox, A. M.; Bradley, D. D. C. *J. Organomet. Chem.* **2002**, *645*, 168.

(13) (a) Grabchev, I.; Moneva, I.; Bojinov, V.; Guittonneau, S. *J. Mater. Chem.* **2000**, *10*, 1291. (b) Zhang, Y. C.; Zhu, W. H.; Wang, W. J.; Tian, H.; Su, J. H.; Wang, W. C. *J. Mater. Chem.*, **2002**, *12*, 1294.

(14) (a) Zhu, W. H.; Tian, H.; Elschner, A. *Chem. Lett.* **1999**, 501. (b) Zhu, W. H.; Hu, M.; Wu, Y. Q.; Tian, H.; Sun, R. G.; Epstein, A. J. *Synth. Met.* **2001**, *119*, 547. (c) Cacialli, F.; Friend, R. H.; Bouche, C. M.; Le Barny, P.; Facoetti, H.; Soyer, F.; Robin, P. J. *J. Appl. Phys.* **1998**, *83*, 2343. (d) Utsugi, K.; Takano, S. J. *J. Electrochem. Soc.* **1992**, *139*, 3610.

(15) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252.

(16) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1287.

(17) Choi, M. S.; Aida, T.; Luo, H. X.; Araki, Y.; Ito. O. *Angew. Chem., Int. Ed.* **2003**, 42, 4060.

(18) (a) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175. (b) Adronov, A.; Malenfant, P. R. L.; Fréchet, J. M. J. *Chem. Mater.* **2000**, *12*, 1463.

(19) Weil, T.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1900.

(20) (a) Förster, T. *Ann. Phys.* **1948**, *2*, 55. (b) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836. (c) Gong, X.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Funct. Mater.* **2003**, *13*, 439.

(21) Banerjee, S.; Wong, S. S. *Nano Lett.* **2002**, *2*, 195.

(22) Hohle, C.; Hofmann, U.; Schloter, S.; Thelakkat, M.; Strohriegl, P.; Haarer, D.; Zilker, S. J. *J. Mater. Chem.* **1999**, *9*, 2205.

(23) Satoh, N.; Cho, J. S.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.

(24) (a) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1. (b) O'Brien, D. F.; Burrows, P. E.; Forrest, S. R.; Konne, B. E.; Loy, D. E.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1108. (c) Konne, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235.

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