

Synthesis of Carrier-Transporting Dendrimers with Perylenebis(dicarboximide)s as a Luminescent Core

Jianfeng Pan,^[a] Weihong Zhu,^{*[a]} Shangfeng Li,^[a] Jun Xu,^[a] and He Tian^{*[a]}

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Well-defined, modular dendrimers enable processing techniques and electronic properties to be tuned independently. Moreover, the dendritic topology can isolate the core chromophore, thus reducing or eliminating strong intermolecular interactions. This paper presents the synthesis of three series of flexible, dendron-functionalized dendrimers as red-light-emitting materials by a convergent approach: (1) carbazole (CZ) or oxadiazole (OXZ) terminated imide-type dendrimers, (2) cascade energy-transferring imide-type dendrimers, and (3) CZ-terminated perylene bay-type dendrimers. They all consist of the luminescent core of perylenebis(dicarboximide)s with specific functional groups of CZ or OXZ at the periphery and are constructed from flexible Fréchet-type poly(aryl ether) dendrons. The chemical structures of the dendrons and dendrimers were determined by standard spectroscopic

techniques including ^1H and ^{13}C NMR spectroscopy and low/high-resolution mass spectrometry (ESI or MALDI-TOF). The dendrimers are designed on the basis of the following considerations: (1) dendron functionalization to incorporate CZ or OXZ units to realize the carrier-injection adjustment, (2) tuning or improving solubility, functionality, glass-transition temperature (T_g) with well-defined dendrons, and (3) avoiding luminescence quenching with the help of high site-isolation of dendrons to enhance core luminescence. DSC results indicate that the incorporation of Fréchet-type poly(aryl ether) dendrons can improve the amorphous properties and increase T_g .

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Introduction

Organic light-emitting diodes (OLEDs) have received a huge amount of scientific and industrial attention since their discovery in 1987 because of their potential applications in large-area, flat-panel displays.^[1–3] Although much progress has been made over the past decades,^[4,5] full-color OLEDs still remain to be improved in terms of efficiency, color purity, durability, as well as manufacturing process and cost, which, in turn, rely on the evolution of high performance OLED materials, including RGB emitters. Of the three primary colors required in a full-color device, green-light-emitting materials have already been achieved with high brightness and efficiency, while red- and blue-light-emitting materials fully meeting the requirements for commercial application are scarce.^[6,7] There are only a few red dopant emitters, including pyran-containing compounds,^[8,9] europium chelate complexes,^[10–12] and porphyrin compounds.^[13] However, all these fluorophores possess a highly concentration-dependent emission, and have an inherent tendency to aggregate due to either attractive dipole–

dipole interactions or effective intermolecular π -stacking, thus becoming either weakly emissive or nonemissive in the solid state.^[14,15] For a practical application it is necessary to develop highly promising host-emitting nondoped red emitters, instead of the above-mentioned red dopant emitters, to overcome the difficult reproducibility of the optimum doping level in devices fabricated by vacuum deposition.^[6]

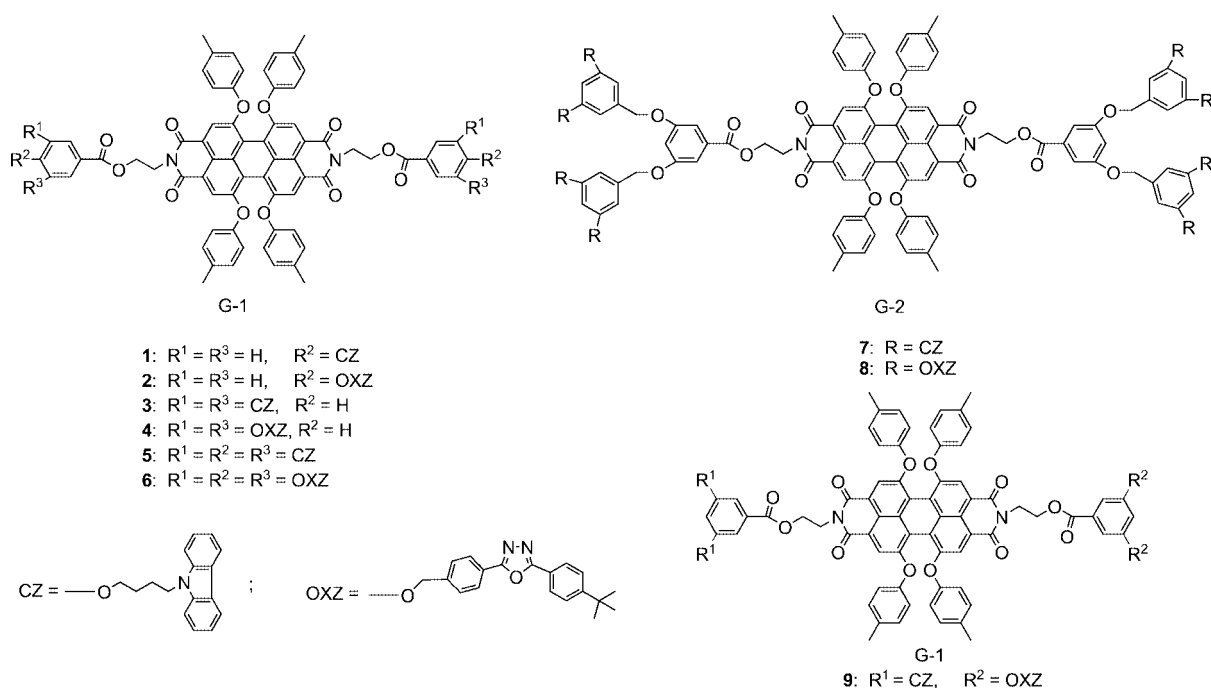
In this regard, dendrimers^[16] should be a good alternative to overcome the attractive dipole–dipole interactions or effective intermolecular π -stacking. Luminescent dendrimers consist of three main units: an emissive core, dendrons, and terminal or peripheral groups. In general, well-defined dendrimers have good amorphous properties and high solubility, which makes the fabrication of thin films by the spin-coating method easier. Such well-defined, modular construction enables the processing and electronic properties to be tuned independently. Moreover, the dendritic topology can isolate the core chromophore, thus reducing or eliminating strong intermolecular interactions.^[17] A number of dendrimers have been applied in OLEDs.^[18–20] Recently, a class of rigid polyphenylene dendrimers based on the chromophore of perylenebis(dicarboximide)s have been studied by Müllen et al. Those dendrimers show good solubility and film-forming properties, and display strong red-orange photoluminescence with decreasing chromophore interactions, although the efficiencies of devices fabricated

[a] Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China
Fax: +86-21-6425-2288
E-mail: tianhe@ecust.edu.cn
whzhu@ecust.edu.cn

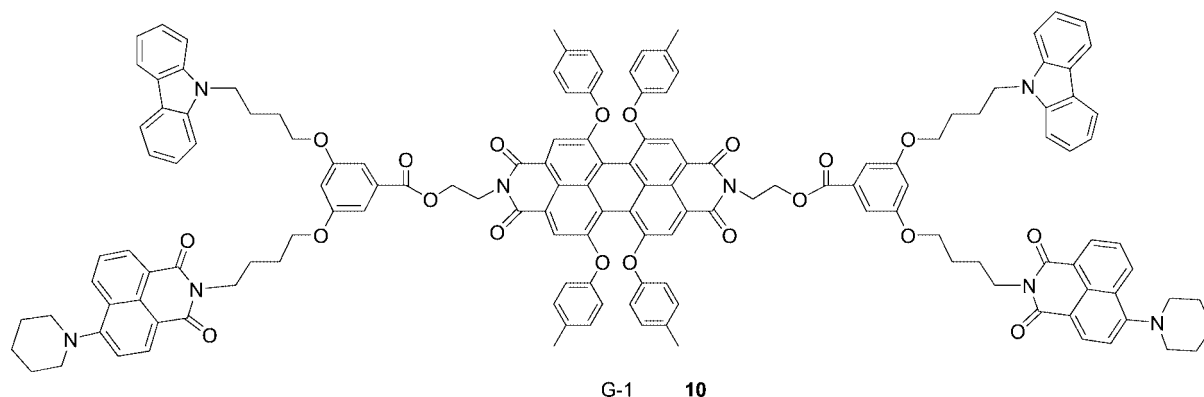
with these materials were still low due to poor charge-transport through the dendritic shell.^[21,22]

We have previously reported a class of naphthalenedicarboximide dendrimers exhibiting specific light-harvesting and carrier injection-tuning properties,^[23] and herein we extend this work to present the synthesis of three series of flexible dendron-functionalized dendrimers as red-light-emitting materials by a convergent approach: (1) carbazole (CZ) or oxadiazole (OXZ) terminated imide-type dendrimers, (2) cascade energy-transferring imide-type dendrimers, and (3) CZ-terminated bay-type dendrimers (shown in Schemes 1, 2, and 3, respectively). They are characteristic of the luminescent core of perylenebis(dicarboximide)s with specific functional groups (CZ or OXZ) at the periphery

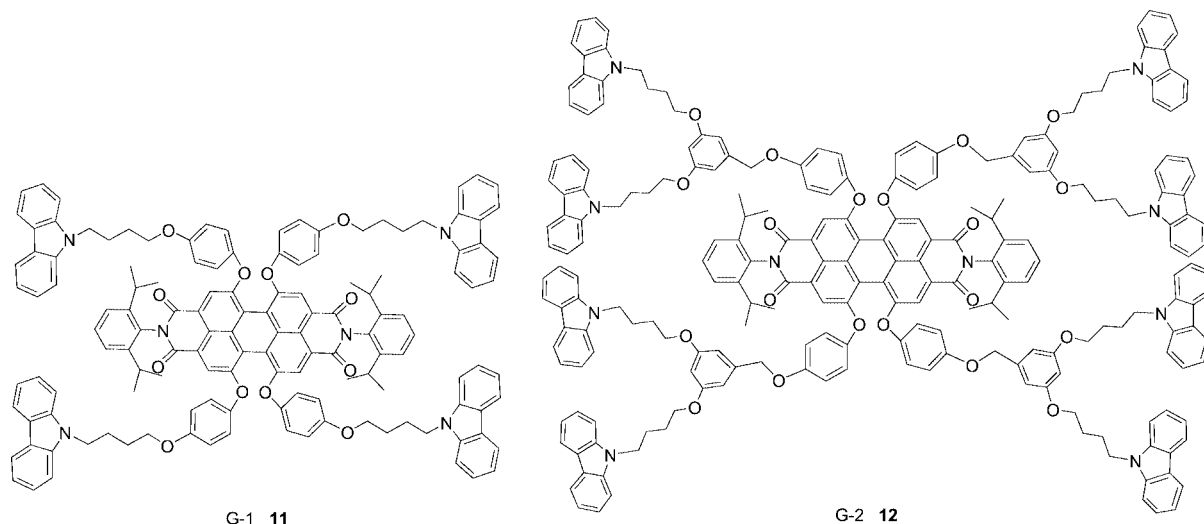
constructed by flexible Fréchet-type poly(aryl ether) dendrons. The incorporated CZ or OXZ units can play a major role in improving both carrier-transport injection and light-harvesting for the core chromophores. Notably, by taking advantage of the well-aligned energy level of carbazole–naphthalenedicarboximide–perylenebis(dicarboximide) fluorophores, the naphthalenedicarboximide unit can play a role in cascade energy-transfer from the carbazole to the core perylenebis(dicarboximide) unit. We expect that such a design strategy of using cascade energy-transfer, site-isolation, and light-harvesting of the functionalized dendrons might conceptually lead to the development of novel promising host-emitting nondoped red emitters based on perylenebis(dicarboximide)s for use in OLEDs.



Scheme 1. Chemical structures of CZ- or OXZ-terminated imide-type dendrimers.



Scheme 2. Chemical structure of cascade energy-transfer imide-type dendrimers.



Scheme 3. Chemical structures of CZ-terminated bay-type dendrimers.

Results and Discussion

Synthesis of CZ- or OXZ-Terminated Imide-Type Dendrimers by a Convergent Approach

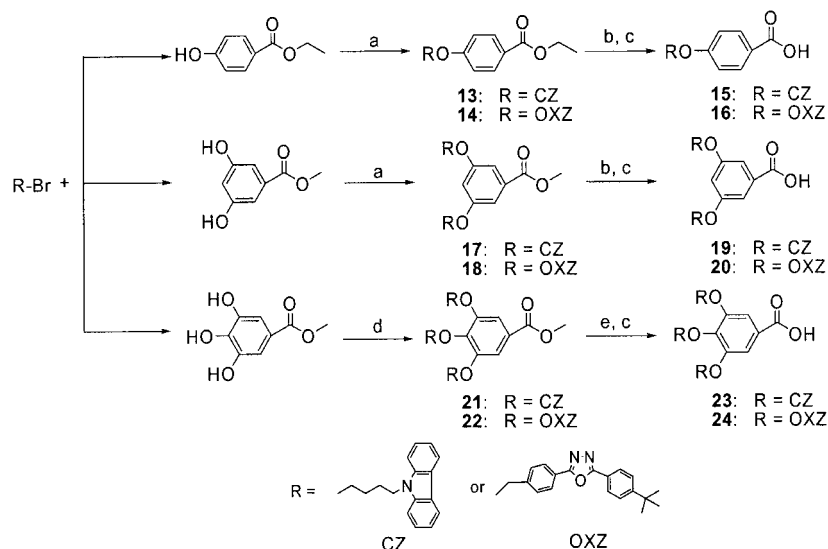
Dendrimers provide new opportunities for precisely placing charge-carrier transporting units by generations in a three-dimensional, nanoscale construction. The dendritic architecture can also be used to improve the solubility of luminescent chromophores to form uniform films by the spin-coating technique, thus overcoming the high cost of the vacuum-deposition process. In spite of the impressive control of solubility and amorphous form,^[23,24] the design of modulating charge-carrier-transporting dendrimers for OLED applications is so far rare.^[25] In line with our ongoing efforts on studying multi-chromophoric emitters containing a carrier-transporting unit as the EL active layer for optimized device performance,^[23,26] we designed a series of novel dendrimers with different generations by a convergent synthetic approach on the basis of the following considerations: (1) dendron functionalization, (2) incorporating CZ or OXZ units to tune carrier injection, (3) tuning or improving solubility, functionality, and glass-transition temperature (T_g) with well-defined dendrons, and (4) avoiding core luminescence quenching with the help of high dendron site-isolation to enhance the core luminescence.

As shown in Scheme 1, the synthesized imide-type dendrimers (**1–9**) contain CZ or OXZ units as specific functional groups at the periphery, Fréchet-type poly(aryl ether)s as the nonconjugated dendrons, and perylenebis(dicarboximide)s as the chromophore core. Perylenebis(dicarboximide)s are well-known red emitters with high fluorescence quantum yields and outstanding chemical, thermal, and photochemical stability, and their derivatives have been widely applied in organic molecular electronics.^[27] The synthesis of these dendrimers proceeded in a modular fashion using the convergent approach originally reported by Hawker and Fréchet.^[28] Two simple synthetic transformations were used for synthesizing the dendrons: (1) selective

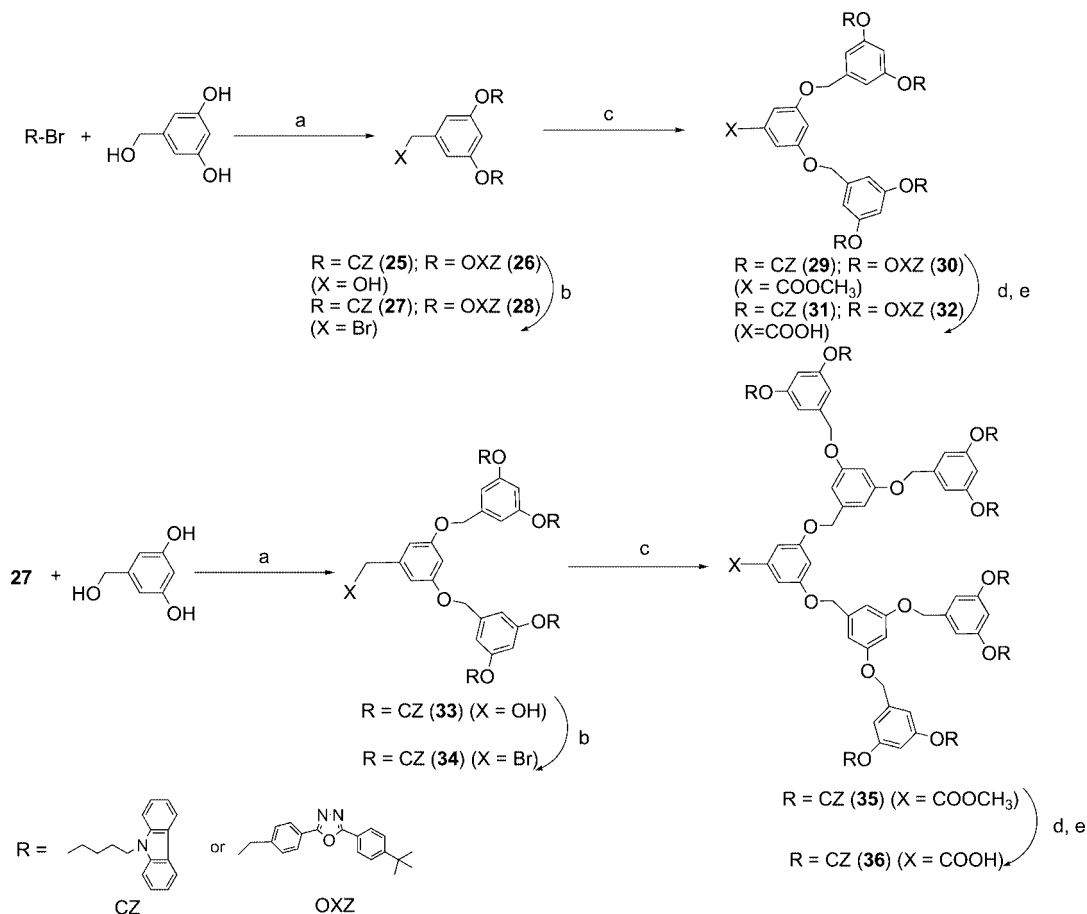
alkylation of phenolic hydroxy groups, and (2) conversion of a benzylic alcohol into a benzylic bromide to generate a reaction focus. In other words, the perylenebis(dicarboximide) core containing two hydroxy groups and poly(aryl ether) dendrons bearing CZ or OXZ units were synthesized separately and then assembled in the last step. The core chromophore of perylenebis(dicarboximide)s was prepared in four steps starting from 1,6,7,12-tetrachloro-3,4,9,10-perylenebis(dicarboxylic anhydride).^[29] To increase the solubility in common organic solvents, phenoxy groups were introduced into the parent structure of the perylenebis(dicarboximide)s.

Facile functional-group manipulation at the periphery allowed the attachment of specific units of carbazoles and oxadiazoles, which are widely used in OLEDs as hole- and electron-transporting units, respectively. The convergent assembly of three different generation-dendrons containing carrier-transporting units is outlined in Schemes 4 and 5. Treatment of *N*-(4-bromobutyl)-9*H*-carbazole or 2-[4-(bromomethyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole with ethyl 4-hydroxybenzoate in the presence of K_2CO_3 and 18-crown-6 in acetone under argon yielded (CZ)₁-(G-1)-COOC₂H₅ (**13**) or (OXZ)₁-(G-1)-COOC₂H₅ (**14**), whose hydrolysis gave the G-1 dendrons (CZ)₁-(G-1)-COOH (**15**) or (OXZ)₁-(G-1)-COOH (**16**). Similarly, compounds **17**, **18**, **21**, and **22** were obtained in good yields when *N*-(4-bromobutyl)-9*H*-carbazole or 2-[4-(bromomethyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole was treated with methyl 3,5-dihydroxybenzoate or methyl gallate in acetone at reflux. Subsequent hydrolysis of these compounds resulted in G-1 dendrons (**19**, **20**, **23**, and **24**; Scheme 4). These G-1 dendrons contain one to three carrier-transporting units (CZ or OXZ). We used the phenolic hydroxy groups of the initial benzoate to control the number of carrier-transporting units introduced onto the resulting G-1 dendrons.

Similarly, the G-2 dendrons **31** and **32** and G-3 dendron **36** can be obtained by repeating the alkylation of the phe-



Scheme 4. Synthetic route to G-1 dendrons of imide-type dendrimers. Reagents and conditions: a) K_2CO_3 , 18-crown-6, acetone, reflux, 60 h; b) KOH, THF/methanol, reflux, 10 h; c) 10% HCl; d) K_2CO_3 , 18-crown-6, THF, reflux, 60 h; e) KOH, THF/methanol, reflux, 16 h.



Scheme 5. Synthetic route to G-2 and G-3 dendrons of imide-type dendrimers. Reagents and conditions: a) K_2CO_3 , 18-crown-6, acetone, reflux, 60 h; b) $CBBr_4/PPh_3$, CH_2Cl_2 ; c) methyl 3,5-dihydroxybenzoate, K_2CO_3 , 18-crown-6, THF, reflux, 60 h; d) KOH, THF/methanol, reflux; e) 10% HCl.

nolic hydroxy groups and transformation of the benzylic alcohol into benzylic bromide (shown in Scheme 5). Bromination of the benzylic alcohol group by treatment with carbon tetrabromide/triphenylphosphane in CH_2Cl_2 at room

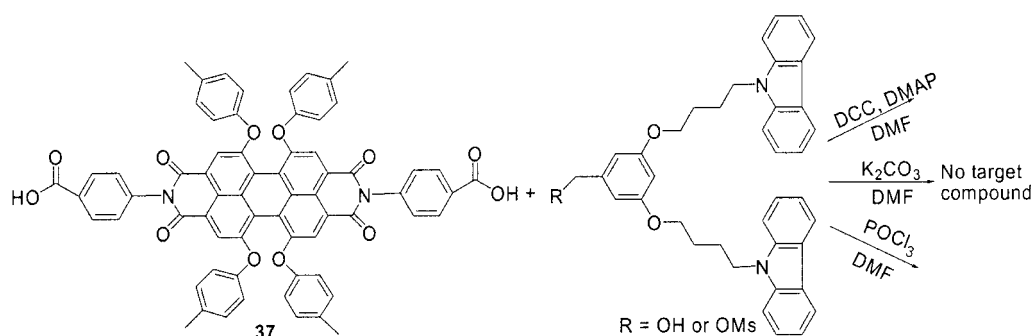
temperature proceeded smoothly to afford the corresponding bromide. In this step, the amount of $CBBr_4/PPh_3$ had to be increased with each generation to ensure complete conversion. The dendritic structures of G-2 and G-3 are

carrier-transporting-unit-terminated with the characteristic Fréchet-type poly(aryl ether) dendrons based on the combination of 3,5-aryl branching and ethereal connectivity.

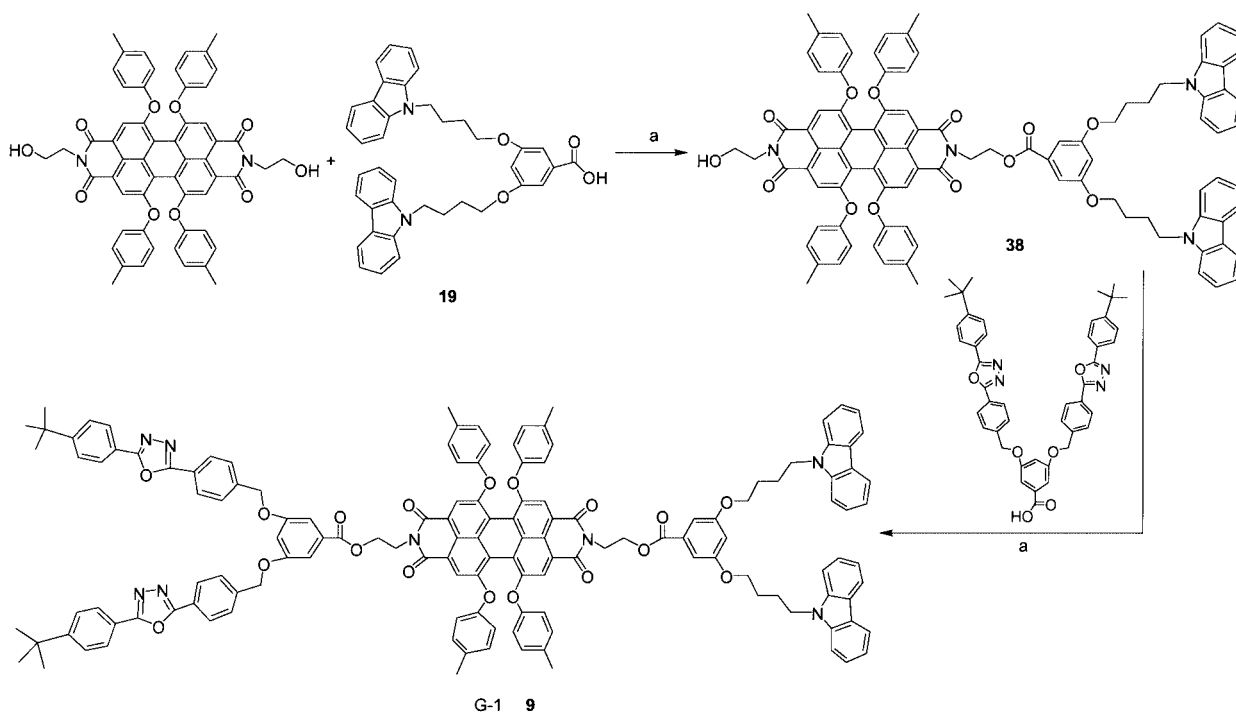
As mentioned above, the perylenebis(dicarboximide) core containing two hydroxy groups and the poly(aryl ether) dendrons of benzoic acid bearing CZ or OXZ units were synthesized separately and then assembled in the last step by esterification. The esterification of a carboxylic acid with an alcohol can be accomplished only if a means is available to drive the equilibrium towards the ester.^[30] In our synthesis, the removal of water by use of a dehydrating agent proved to be successful for the assembly of dendrons with a perylenebis(dicarboximide) core. Thus, dehydration with dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) proceeded in anhydrous CH_2Cl_2 at room temperature with esterification of the core intermediate with the corresponding different generation dendrons to obtain the target dendrimers. They were purified by

chromatography on silica gel and the purity was measured by TLC and HPLC. However, the purification of these dendrimers became more complicated with each generation.

It should be pointed out that we also attempted to prepare the target dendrimers from the reaction between compound **25** and compound **37** by conventional synthetic ester protocols and methods (Scheme 6). In the first route, a mixture of compound **25**, compound **37**, dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) was dissolved in anhydrous DMF and stirred at room temperature for 48 h. Secondly, we attempted to dehydrate a mixture of compounds **25** and **37** in anhydrous DMF, at 100 °C, by titration with fresh POCl_3 . Finally, the tosylation of compound **25** was attempted as this method has proved effective in our synthesis of dendrimers based on 1,8-naphthalenedicarboximide.^[23] Unfortunately, all these reactions failed to afford the desired compound, probably because of the poor solubility of compound **37** in DMF.



Scheme 6. Attempts to synthesize target imide-type dendrimers according to conventional synthetic ester protocols and tosylation.



Scheme 7. Synthetic route to target dendrimer **9**. Reagents and conditions: a) DCC, DMAP, CH_2Cl_2 , room temp., 24 h.

G-1 dendrimer **9**, with both CZ and OXZ units incorporated simultaneously from the imide side, was synthesized similarly. Thus, the core luminescent moiety as well as the hole- and electron-transporting units are assembled together in a single molecule of dendrimer **9**, which can be regarded as a bipolar emitter.^[31,32] Dendrimer **9** was obtained by two esterification steps in a poor 0.6% overall yield (Scheme 7).

Synthesis of Cascade Energy-Transferring Imide-Type Dendrimers

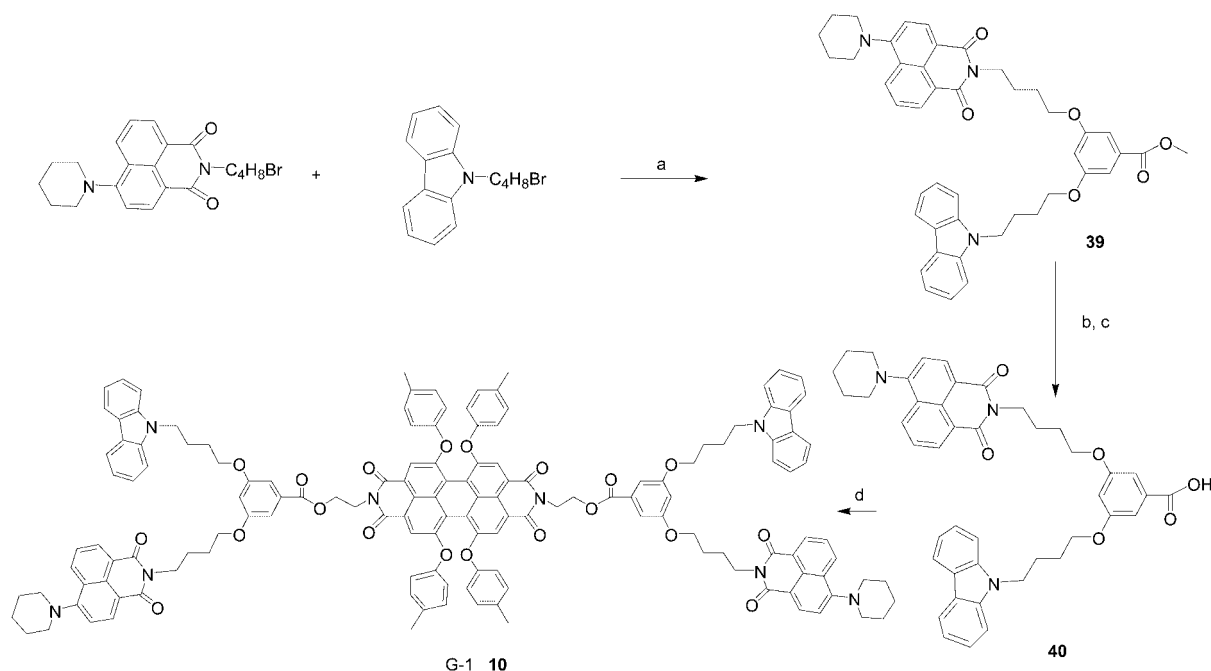
Recently, systems capable of directional Förster resonance energy transfer (FRET) and electron transfer between several chromophores have received much attention.^[33] As shown in Scheme 2, another dendrimer (**10**), whose dendrons contain carrier-transporting carbazole units and additional naphthalenedicarboximide units, was designed and synthesized. Notably, by taking advantage of the well-aligned energy level of carbazole–naphthalenedicarboximide–perylenebis(dicarboximide) fluorophores the naphthalenedicarboximide unit can play a role in cascade energy-transfer from the carbazole to the core perylenebis(dicarboximide) unit because the absorption peak of the naphthalenedicarboximide unit is located between that of the carbazole and perylenebis(dicarboximide) units. A precondition for FRET is the overlap of the donor fluorescence with the acceptor absorption. Consistent with this, FRET is favored from the carbazole unit to the naphthalenedicarboximide unit, and then from the naphthalenedicarboximide unit to the perylenebis(dicarboximide) core, instead of directly from the carbazole unit to the perylene-

bis(dicarboximide) core, due to the smaller spectral overlap between the luminescence spectra of the carbazole unit and the absorption of the perylenebis(dicarboximide) core. This system can be utilized to demonstrate that, with proper chromophore selection, FRET can be more favorable in a vectorial cascade process.

The preparation of dendrimer **10** is similar to that described above. The convergent assemblies are outlined in Scheme 8. Treatment of *N*-(4-bromobutyl)-9*H*-carbazole and *N*-(4-bromobutyl)-4-(piperidin-1-yl)-1,8-naphthalenedicarboximide with methyl 3,5-dihydroxybenzoate in the presence of K_2CO_3 and 18-crown-6 in acetone under argon yielded (CZ)₁-(NP)₁-(G-1)-COOCH₃ (**39**), in 32.9% yield, and hydrolysis of this compound gave the G-1 dendron (CZ)₁-(NP)₁-(G-1)-COOH (**40**). This compound was then coupled to the core intermediate by dehydration with DCC and DMAP in anhydrous CH₂Cl₂ at room temperature to afford dendrimer **10**.

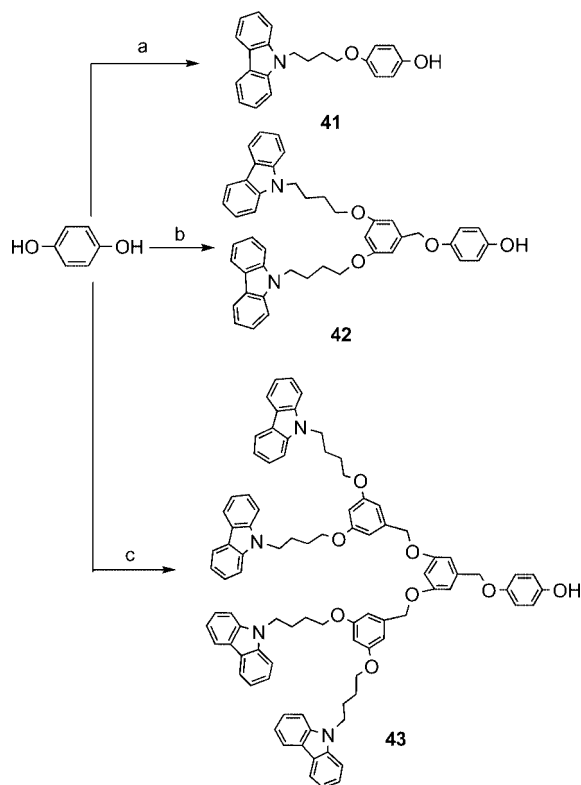
Synthesis of CZ-Terminated Perylene Bay-Type Dendrimers

Two notable and unique properties of functionalized dendrimers are their light-harvesting and site-isolation effects. The site-isolation effect can control the intermolecular interactions and reduce or prevent the aggregation of the core unit, thus alleviating the aggregation problem that is known to be detrimental to device efficiency. To receive a better site-isolation effect than that of imide-type dendrimers, we designed another two bay-type dendrimers whose dendrons are directly incorporated from the ring of the parent perylenebis(dicarboximide) (Scheme 3). The synthesis of



Scheme 8. Synthetic route to target dendrimer **10**. Reagents and conditions: a) methyl 3,5-dihydroxybenzoate, K_2CO_3 , 18-crown-6, THF, reflux, 60 h; b) KOH, THF/methanol, reflux, 20 h; c) 10% HCl; d) *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4,9,10-perylenebis(dicarboximide), DCC, DMAP, CH₂Cl₂, room temp., 24 h.

second-generation dendrons containing carbazole units is outlined in Scheme 9. Treatment of an excess of benzene-1,4-diol with the appropriate intermediates (molar ratio = 10:1) in the presence of K_2CO_3 and 18-crown-6 in acetone resulted in dendrons **41**, **42**, and **43**. Notably, the synthesis of the third-generation (G-3) bay-type dendrimers was not possible due to the increasing steric hindrance of the substituents with each generation.



Scheme 9. Synthetic route to dendrons **41**, **42**, and **43** for the bay-type dendrimers. Reagents and conditions: a) *N*-(4-bromobutyl)-9*H*-carbazole, K_2CO_3 , 18-crown-6, acetone, reflux, 36 h; b) **27**, K_2CO_3 , 18-crown-6, acetone, reflux, 60 h; c) **34**, K_2CO_3 , 18-crown-6, acetone, reflux, 60 h.

Structural Characterization

All the dendrimers obtained are well soluble in common organic solvents such as chlorobenzene, THF, $CHCl_3$, and CH_2Cl_2 . They are stable during normal manipulation and no special handling is required. The chemical structures of the dendrons and dendrimers were determined by standard spectroscopic techniques, including 1H and ^{13}C NMR spectroscopy and low/high-resolution mass spectrometry (ESI or MALDI-TOF) (see Experimental Section). As an example, Figure 1 shows the 1H NMR spectra (500 MHz) of the intermediate dendrons **17** (G-1), **29** (G-2), and **35** (G-3) in $CDCl_3$. Four characteristic signals of the aromatic hydrogen atoms of the carbazole unit are observed at $\delta \approx 7.2$ –8.2 ppm. With increasing generations, the signals assigned to the phenyl protons ($\delta = 6.0$ –7.0 ppm) of the poly(aryl ether) dendrons become more complicated. For instance,

only two signals are observed for dendron **17**, whereas five different signals in the ratio 8:4:4:2:1 are observed in the case of **35**. All integration ratios are exactly proportional to the number of hydrogen atoms. As shown in Figure 2, the ^{13}C NMR spectrum of dendrimer **3** (Scheme 1) shows a complicated peak pattern in the range $\delta = 115$ –160 ppm due to the different environments of the carbon atoms of the aromatic rings of the dendrimers. The signals labeled 1 and 2 at $\delta = 166.313$ and 163.562 ppm are assigned to carbonyl carbon atoms in the dendrimer and signals 23/24 and 25/26 are assigned to aliphatic carbon atoms connected to oxygen and nitrogen atoms, respectively. Finally, the total number of signals is well consistent with the number of carbon atoms in the molecule.

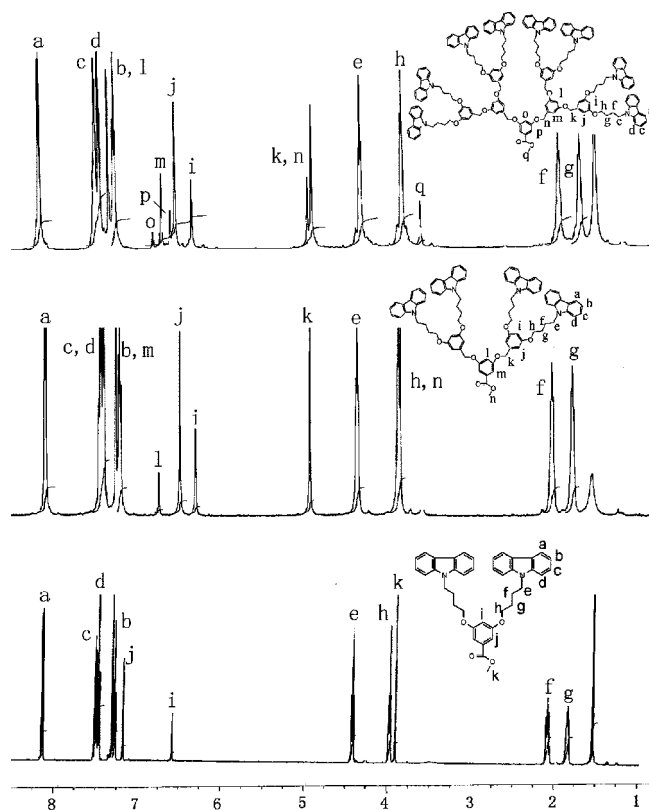


Figure 1. 1H NMR spectra of dendrons **17** (G-1), **29** (G-2), and **35** (G-3).

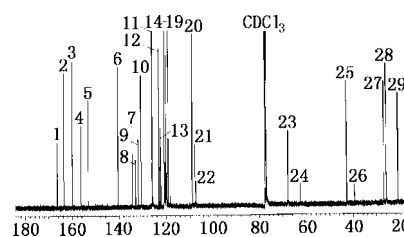


Figure 2. ^{13}C NMR spectrum of dendrimer **3**.

Additional definitive evidence was obtained from the MALDI-TOF mass spectra. All dendrimers show the corresponding molecular ion peaks. For example, the molecular formula of dendrimer **3** is $C_{134}H_{110}N_6O_{16}$. The calculated average for the peak of the molecular ion $[M^+]$ is 2058 and

we observed the corresponding $[M^+]$ peak centered at $m/z = 2058.94$; the peaks centered at $m/z = 2081.95$ and 2097.93 are ascribed to $[M^+ + Na]$ and $[M^+ + K]$, respectively. This is similar to dendrimer **4**, in whose MALDI-TOF mass spectrum $[M^+]$ appears at $m/z = 2336.96$, with the peaks for $[M^+ + Na]$ and $[M^+ + K]$ at $m/z = 2357.93$ and 2373.91 , respectively (see Figure 3). In the MALDI-TOF mass spectrum of dendrimer **12** the peaks for $[M^+ + Na]$ and $[M^+ + K]$ appear at $m/z = 3425.4$ and 3438.4 , respectively.

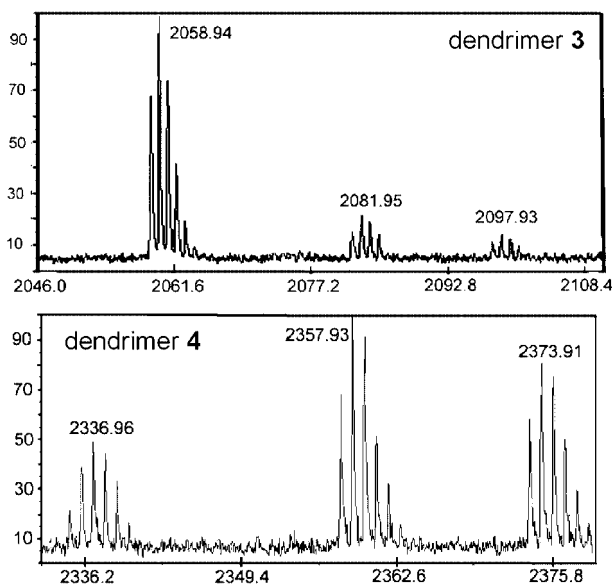


Figure 3. MALDI-TOF mass spectra of dendrimers **3** (top) and **4** (bottom).

Thermal Stability

Dendrimers are generally able to prevent spatial reorientation of molecules, thus eliminating their tendency to recrystallize and favorably increasing their glass-transition temperature (T_g). In our dendrimers, compounds **3** and **4** (G-1) have a higher melting point than the other dendrimers. For instance, the curve of the DSC thermogram for dendrimer **3** (Figure 4) reveals that T_g is at 110.2°C in the heating process. When the compound was cooled at a rate of $10^\circ\text{C min}^{-1}$ from 260 to 30°C no distinct crystallization phase was observed. Broad exothermic peaks due to crystallization were observed at around 162 and 192°C for the first and second heating, respectively, and T_g did not

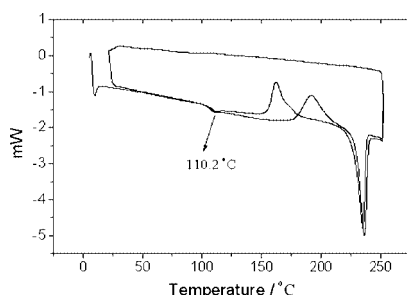


Figure 4. DSC trace of dendrimer **3**.

change in the second heating process. Dendrimer **4** shows a slightly higher T_g at 152.7°C . Thus, the thermal analysis results indicate that such dendron-functionalized luminescent materials have good thermal stability, which is essential for fabricating stable OLEDs.

Absorption and Fluorescent Properties

These 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 the carbazole unit, the absorption peak at around 285 nm is attributed to the oxadiazole unit, and the latter three peaks to the characteristic absorption of the perylenebis(dicarboximide) core (Figure 5). Furthermore, there is a linear increase in the relative absorbance of the carbazole units (330 , 345 nm) in these dendrimers (Figure 5).^[34] The absorbance of the peripheral CZ or OXZ units is clearly proportional to their increased number in each generation, which indirectly reflects the flawless or perfect structures of the synthesized dendrimers. Notably, there is no distinct spectral shift of the absorption band of the peripheral CZ and OXZ units with increasing generation. The absorption intensity of the perylenebis(dicarboximide) core in THF does not change notably with increasing generation but does exhibit a small bathochromic shift, which is attributed to the micro-environment polarity of the larger dendritic wedges. Moreover, with respect to the reference compounds, the absorption spectra of all perylenebis(dicarboximide)-core dendrimers are well matched by the sum of the spectra of the relative constituent chromophores. In all cases the 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 and electron transfers.

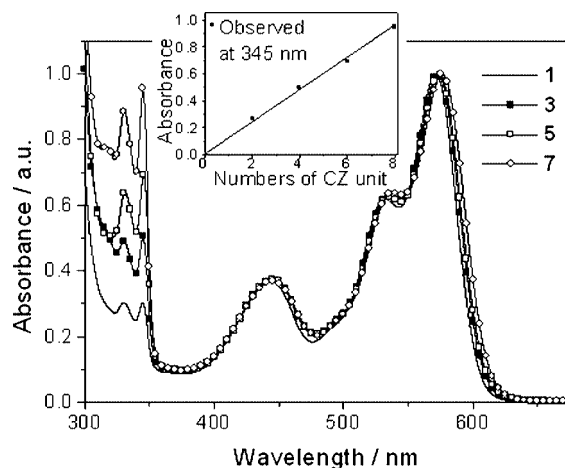


Figure 5. Normalized absorption spectra of dendrimers **1**, **3**, **5**, and **7** in THF ($2.0 \times 10^{-5}\text{ M}$). Inset: Plot of number of carbazole units in dendrimer vs. absorbance at 345 nm .

All synthesized dendrimers **1–12** in THF show characteristic luminescence of the core perylenebis(dicarboximide)

(peak at around 600 nm). Compared with their fluorescence in THF, the fluorescence of the dendrimers in the solid state is red-shifted; for example, the red-shifts of dendrimers **1**, **3**, and **5** are 72, 60, and 51 nm, respectively (see Figure 6). These results indicate that a higher-generation dendrimer has a relatively smaller Stokes shift than a lower-generation one, which is indicative of a certain degree of site isolation or dendron dilution, which reduces or prevents the aggregation of the core.

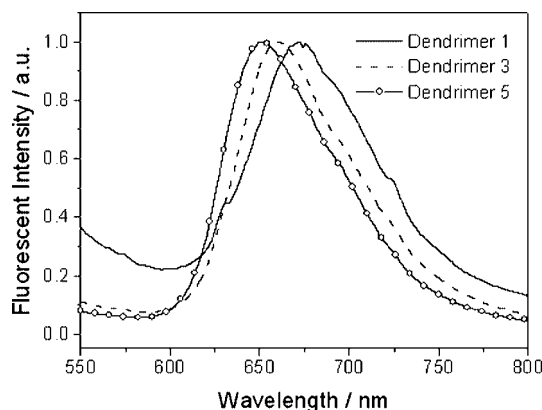


Figure 6. Normalized fluorescence spectra of dendrimers **1**, **3**, and **5** in solid film excited at 460 nm.

The interactions between the peripheral units and the perylenebis(dicarboximide) core in the dendrimers were also studied by steady-state and time-resolved fluorescence spectroscopy under both direct and indirect excitation. Because perylenebis(dicarboximide) derivatives have a high electron affinity [3.9 eV for the LUMO energy of the core perylenebis(dicarboximide)],^[27b] photo-induced electron transfer (PIET) occurs from the low-oxidation-potential units of the carbazole to the perylenebis(dicarboximide) core. Preliminary results show that two different phenomena exist: no enhanced core fluorescence for dendrimers bearing carbazole units is observed because the energy transfer or light-harvesting of the peripheral carbazole is counteracted by PIET, while enhanced core fluorescence arising from the energy transfer or light-harvesting of peripheral oxadiazole is observed for dendrimers bearing these units as no PIET can take place because of the high electron affinity of the oxadiazole and perylenebis(dicarboximide). Further studies of photoinduced energy and electron transfers and EL device performances are now underway, and will be reported elsewhere.

Conclusions

Different generations of three novel series of dendrimers for red-light emission that contain perylenebis(dicarboximide) cores, Fréchet-type poly(aryl ether) dendrons, and peripheral functional units such as carbazole or oxadiazole have been designed and synthesized. Two simple synthetic transformations have been used to synthesize the dendrons, namely selective alkylation of phenolic hydroxy groups and conversion of a benzylic alcohol into a benzylic bromide to

generate a reaction focus. Esterification of the core intermediate with the corresponding different generation dendrons promoted by dehydration with dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) was easily achieved in anhydrous CH_2Cl_2 at room temperature to obtain the target dendrimers. All dendrimers have good solubility and thermal stability, and could be applied as promising active red luminescent emitters with carrier-transport ability in OLEDs.

Experimental Section

General Information: Commercially available reagents were used without further purification unless noted otherwise. Solvents were purified by common methods. The starting materials 2-[4-(bromomethyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole,^[35] *N*-(4-bromobutyl)-9*H*-carbazole,^[36] and *N*-(4-bromobutyl)-4-(piperidin-1-yl)-1,8-naphthalenedicarboximide^[37] were prepared according to literature procedures. Melting points were measured with an X4 micro-melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with a Bruker AM-500 spectrometer. Mass spectra were recorded using the ESI or MALDI-TOF techniques with α -cyano-4-hydroxycinnamic acid as matrix. HPLC was carried out with an Agilent 1100 LC system. Glass-transition temperatures (T_g) were measured with a differential scanning calorimeter (TA DSC 2910) at a scan rate of $10\text{ }^\circ\text{Cmin}^{-1}$. Absorption and fluorescence spectra were recorded with a Varian Cary 500 and a Varian Cary Eclipse spectrometer, respectively.

Ethyl 4-[4-(9*H*-Carbazol-9-yl)butoxy]benzoate [(CZ)₁-(G-1)-CO-OC₂H₅, **13]:** A mixture of 9-(4-bromobutyl)-9*H*-carbazole (1.0 g, 3.3 mmol), ethyl 4-hydroxybenzoate (0.6 g, 3.6 mmol), anhydrous potassium carbonate (1.2 g, 8.7 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 ($3 \times 30\text{ mL}$). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (2:1) to give **13** as a white solid (1.1 g, yield 85.9%). M.p. $84\text{--}85\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$): δ = 1.45 (t, J = 7.2 Hz, 3 H, $-\text{CH}_3$), 1.88 (m, 2 H, $-\text{CH}_2-$), 2.10 (m, 2 H, $-\text{CH}_2-$), 3.95 (t, J = 6.1 Hz, 2 H, $-\text{OCH}_2-$), 4.36 (m, 2 H, $-\text{OCH}_2-$), 4.40 (t, J = 7.0 Hz, 2 H, $-\text{NCH}_2-$), 6.82 (d, J = 8.9 Hz, 2 H, Ph-H), 7.20 [t, J = 7.0 Hz, 2 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.6, J = 8.0 Hz, 4 H, Ph-H (CZ)], 7.95 (d, J = 8.7 Hz, 2 H, Ph-H), 8.12 [d, J = 7.6 Hz, 2 H, Ph-H (CZ)] ppm.

(OXZ)₁-(G-1)-COOC₂H₅ (14**):** A mixture of 2-[4-(bromomethyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (1.5 g, 4.0 mmol), ethyl 4-hydroxybenzoate (0.8 g, 4.8 mmol), anhydrous potassium carbonate (1.6 g, 11.6 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 ($3 \times 30\text{ mL}$). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (4:1) to give **14** as a white solid (1.6 g, yield 87.0%). M.p. $76\text{--}77\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$):

δ = 1.38 (m, 12 H, -CH₃), 4.30 (m, 2 H, -OCH₂-), 5.23 (s, 2 H, -OCH₂-), 7.07 (d, J = 8.7 Hz, 2 H, Ph-H), 7.58 [t, J = 8.4 Hz, 4 H, Ph-H (OXZ)], 7.96 (d, J = 8.8 Hz, 2 H, Ph-H), 8.01 [d, J = 8.7 Hz, 2 H, Ph-H (OXZ)], 8.10 [d, J = 8.3 Hz, 2 H, Ph-H (OXZ)] ppm.

4-[4-(9H-Carbazol-9-yl)butoxy]benzoic Acid [(CZ)₁-(G-1)-COOH, 15]: A mixture of compound **13** (1.1 g, 2.8 mmol) and KOH (3.8 g, 67.2 mmol) in tetrahydrofuran/methanol (15 mL/30 mL) was refluxed with vigorous stirring for 10 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was acidified with 10% aqueous HCl solution (300 mL), then the precipitate was filtered and washed with ethanol to give **15** as a white solid (1.0 g, yield 98.1%). The product was used directly in the next reaction without further purification. M.p. 178–180 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.87 (m, 2 H, -CH₂-), 2.10 (m, 2 H, -CH₂-), 3.90 (t, J = 6.1 Hz, 2 H, -OCH₂-), 4.40 (t, J = 7.1 Hz, 2 H, -NCH₂-), 6.82 (d, J = 8.8 Hz, 2 H, Ph-H), 7.20 [t, J = 7.1 Hz, 2 H, Ph-H (CZ)], 7.40–7.50 [m, 4 H, Ph-H (CZ)], 7.95 (d, J = 8.6 Hz, 2 H, Ph-H), 8.11 [d, J = 7.5 Hz, 2 H, Ph-H (CZ)] ppm.

(OXZ)₁-(G-1)-COOH (16): A mixture of compound **14** (1.6 g, 3.5 mmol) and KOH (2.5 g, 44.6 mmol) in tetrahydrofuran/methanol (30 mL/15 mL) was refluxed with vigorous stirring for 10 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (300 mL). The precipitate was filtered off and washed with ethanol to give **16** as a white solid (1.4 g, yield 93.4%). The product was used directly in the next reaction without further purification. M.p. 158–160 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.38 (s, 9 H, -CH₃), 5.25 (s, 2 H, -OCH₂-), 7.07 (d, J = 8.6 Hz, 2 H, Ph-H), 7.58 [m, 4 H, Ph-H (OXZ)], 7.96–8.02 [m, 4 H, Ph-H, Ph-H (OXZ)], 8.12 [d, J = 7.5 Hz, 2 H, Ph-H (OXZ)] ppm.

Methyl 3,5-Bis[4-(9H-carbazol-9-yl)butoxy]benzoate [(CZ)₂-(G-1)-COOCH₃, 17]: A mixture of *N*-(4-bromobutyl)-9H-carbazole (5.0 g, 16.5 mmol), methyl 3,5-dihydroxybenzoate (1.2 g, 7.1 mmol), anhydrous potassium carbonate (5.9 g, 42.8 mmol), and 18-crown-6 (0.8 g, 2.8 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was then partitioned between CH₂Cl₂ and H₂O and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried with anhydrous MgSO₄ and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH₂Cl₂/CCl₄ (2:1) to give **17** as a white solid (4.1 g, yield 94.2%). M.p. 140–142 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.87 (m, 4 H, -CH₂-), 2.08 (m, 4 H, -CH₂-), 3.88 (s, 3 H, -OCH₃), 3.95 (t, J = 6.0 Hz, 4 H, -OCH₂-), 4.40 (t, J = 7.0 Hz, 4 H, -NCH₂-), 6.54 (s, 1 H, Ph-H), 7.13 (s, 2 H, Ph-H), 7.20 [t, J = 7.4 Hz, 4 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.7, J = 8.1 Hz, 8 H, Ph-H (CZ)], 8.12 [d, J = 7.8 Hz, 4 H, Ph-H (CZ)] ppm.

(OXZ)₂-(G-1)-COOCH₃ (18): A mixture of 2-[4-(bromomethyl)-phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (6.6 g, 17.7 mmol), methyl 3,5-dihydroxybenzoate (1.36 g, 8.1 mmol), anhydrous potassium carbonate (5.0 g, 36.2 mmol), and 18-crown-6 (0.8 g, 2.8 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH₂Cl₂ and H₂O and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were dried with anhydrous MgSO₄ and the solvents evaporated. The product was purified by column

chromatography on silica gel eluting with CH₂Cl₂/CCl₄ (4:1) to give **18** as a white solid (5.2 g, yield 85.6%). M.p. 124–125 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.37 (s, 18 H, -CH₃), 3.90 (s, 3 H, -OCH₃), 5.20 (s, 4 H, -OCH₂-), 6.77 (s, 1 H, Ph-H), 7.30 (s, 2 H, Ph-H), 7.52–7.68 [dd, J = 8.0, J = 8.3 Hz, 8 H, Ph-H (OXZ)], 8.05 [d, J = 8.2 Hz, 4 H, Ph-H (OXZ)], 8.20 [d, J = 8.0 Hz, 4 H, Ph-H (OXZ)] ppm.

3,5-Bis[4-(9H-carbazol-9-yl)butoxy]benzoic Acid [(CZ)₂-(G-1)-COOH, 19]: A mixture of compound **17** (4.1 g, 6.7 mmol) and KOH (3.8 g, 67.2 mmol) in tetrahydrofuran/methanol (30 mL/60 mL) was refluxed with vigorous stirring for 10 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **19** as a white solid (3.8 g, yield 95.9%). The product was used directly in the next reaction without further purification. M.p. 179–181 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.72 (m, 4 H, -CH₂-), 2.10 (m, 4 H, -CH₂-), 3.90 (t, J = 6.0 Hz, 4 H, -OCH₂-), 4.40 (t, J = 7.0 Hz, 4 H, -NCH₂-), 6.54 (s, 1 H, Ph-H), 7.17 (s, 2 H, Ph-H), 7.22 [t, J = 6.9 Hz, 4 H, Ph-H (CZ)], 7.38–7.50 [m, 8 H, Ph-H (CZ)], 8.10 [d, J = 7.4 Hz, 4 H, Ph-H (CZ)] ppm.

(OXZ)₂-(G-1)-COOH (20): A mixture of compound **18** (5.0 g, 6.7 mmol) and KOH (4.0 g, 71.4 mmol) in tetrahydrofuran/methanol (80 mL/40 mL) was refluxed with vigorous stirring for 10 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **20** as a white solid (4.4 g, yield 89.2%). The product was used directly in the next reaction without further purification. M.p. 138–140 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.38 (s, 18 H, -CH₃), 5.19 (s, 4 H, CH₂-), 6.89 (s, 1 H, Ph-H), 7.39 (s, 2 H, Ph-H), 7.54–7.63 [dd, J = 8.0, J = 8.3 Hz, 8 H, Ph-H (OXZ)], 8.05 [d, J = 8.2 Hz, 4 H, Ph-H (OXZ)], 8.18 [d, J = 7.9 Hz, 4 H, Ph-H (OXZ)] ppm.

Methyl 3,4,5-Tris[4-(9H-carbazol-9-yl)butoxy]benzoate [(CZ)₃-(G-1)-COOCH₃, 21]: A mixture of *N*-(4-bromobutyl)-9H-carbazole (3.8 g, 12.6 mmol), methyl gallate (0.6 g, 3.3 mmol), anhydrous potassium carbonate (3.0 g, 21.7 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was partitioned between CH₂Cl₂ and H₂O. The aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL), the combined organic layers were dried with anhydrous MgSO₄, and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH₂Cl₂/CCl₄ (2:1) to give **21** as a white solid (2.5 g, yield 89.4%). M.p. 89–91 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 1.67 (m, 2 H, -CH₂-), 1.72 (m, 4 H, -CH₂-), 1.97 (m, 6 H, -CH₂-), 3.86 (m, 5 H, -OCH₂-, -OCH₃), 3.92 (t, J = 6.1 Hz, 4 H, -OCH₂-), 4.12 (t, J = 7.3 Hz, 2 H, -NCH₂-), 4.22 (t, J = 7.0 Hz, 4 H, -NCH₂-), 7.22 [m, 8 H, Ph-H, Ph-H (CZ)], 7.25 [t, J = 7.4 Hz, 2 H, Ph-H (CZ)], 7.28 [d, J = 8.2 Hz, 4 H, Ph-H (CZ)], 7.38 [m, 6 H, Ph-H (CZ)], 8.10 [m, 6 H, Ph-H (CZ)] ppm.

(OXZ)₃-(G-1)-COOCH₃ (22): A mixture of 2-[4-(bromomethyl)-phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (2.9 g, 7.8 mmol), methyl gallate (0.45 g, 2.4 mmol), anhydrous potassium carbonate (2.0 g, 14.5 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (60 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure, the residue was parti-

tioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (4:1) to give **22** as a white solid (1.2 g, yield 46.5%). M.p. 174–175 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.33 (s, 9 H, $-\text{CH}_3$), 1.38 (s, 18 H, $-\text{CH}_3$), 3.90 (s, 3 H, $-\text{OCH}_3$), 5.25 (s, 6 H, $-\text{OCH}_2-$), 7.43 (s, 2 H, Ph-H), 7.52 [d, J = 8.5 Hz, 2 H, Ph-H (OXZ)], 7.56 [d, J = 8.5 Hz, 4 H, Ph-H (OXZ)], 7.60 [t, J = 8.5 Hz, 6 H, Ph-H (OXZ)], 8.01 [d, J = 8.4 Hz, 2 H, Ph-H (OXZ)], 8.06 [d, J = 8.5 Hz, 6 H, Ph-H (OXZ)], 8.16 [d, J = 8.3 Hz, 4 H, Ph-H (OXZ)] ppm.

3,4,5-Tris[4-(9H-carbazol-9-yl)butoxy]benzoic Acid [(CZ)₃-(G-1)-COOH, 23]: A mixture of compound **21** (2.3 g, 2.7 mmol) and KOH (4.0 g, 71.4 mmol) in tetrahydrofuran/methanol (20 mL/40 mL) was refluxed with vigorous stirring for 16 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **23** as a white solid (2.1 g, yield 94.7%). The product was used directly in the next reaction without further purification. M.p. 85–86 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.58 (m, 2 H, $-\text{CH}_2-$), 1.76 (m, 4 H, $-\text{CH}_2-$), 1.97 (m, 6 H, $-\text{CH}_2-$), 3.88 (t, J = 6.0 Hz, 2 H, $-\text{OCH}_2-$), 3.92 (t, J = 6.0 Hz, 4 H, $-\text{OCH}_2-$), 4.13 (t, J = 7.2 Hz, 2 H, $-\text{NCH}_2-$), 4.22 (t, J = 7.0 Hz, 4 H, $-\text{NCH}_2-$), 7.20 [m, 8 H, Ph-H, Ph-H (CZ)], 7.23 [m, 2 H, Ph-H (CZ)], 7.29 [d, J = 8.1 Hz, 4 H, Ph-H (CZ)], 7.39 [m, 6 H, Ph-H (CZ)], 8.08 [m, 6 H, Ph-H (CZ)] ppm. MS (ESI): m/z = 856.4 [M^+ + Na].

(OXZ)₃-(G-1)-COOH (24): A mixture of compound **22** (1.2 g, 1.1 mmol) and KOH (1.0 g, 17.9 mmol) in tetrahydrofuran/methanol (40 mL/20 mL) was refluxed with vigorous stirring for 16 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (150 mL). The precipitate was filtered off and washed with ethanol to give **24** as a white solid (1.1 g, yield 93.0%). The product was used directly in the next reaction without further purification. M.p. 149–151 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.32 (s, 9 H, $-\text{CH}_3$), 1.38 (s, 18 H, $-\text{CH}_3$), 5.25 (s, 6 H, $-\text{OCH}_2-$), 7.43–7.56 [m, 8 H, Ph-H, Ph-H (OXZ)], 7.60 [t, J = 7.5 Hz, 6 H, Ph-H (OXZ)], 8.01–8.06 [m, 8 H, Ph-H (OXZ)], 8.16 [d, J = 7.8 Hz, 4 H, Ph-H (OXZ)] ppm. MS (ESI): m/z = 1041.4 [M^+].

3,5-Bis[4-(9H-carbazol-9-yl)butoxy]phenylmethanol [(CZ)₂-(G-1)-CH₂OH, 25]: A mixture of *N*-(4-bromobutyl)-9H-carbazole (4.4 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), anhydrous potassium carbonate (3.4 g, 24.6 mmol), and 18-crown-6 (0.8 g, 2.8 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **25** as a white solid (3.44 g, yield 82.8%). M.p. 118–120 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 4 H, $-\text{CH}_2-$), 2.10 (m, 4 H, $-\text{CH}_2-$), 3.85 (t, J = 6.1 Hz, 4 H, $-\text{OCH}_2-$), 4.37 (t, J = 7.1 Hz, 4 H, $-\text{NCH}_2-$), 4.70 (s, 2 H, $-\text{CH}_2\text{OH}$), 6.25 (s, 1 H, Ph-H), 6.50 (s, 2 H, Ph-H), 7.20 [t, J = 6.8 Hz, 4 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.9, J = 8.0 Hz, 8 H, Ph-H (CZ)], 8.20 [d, J = 7.8 Hz, 4 H, Ph-H (CZ)] ppm.

(OXZ)₂-(G-1)-CH₂OH (26): A mixture of 2-[4-(bromomethyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (5.4 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), anhydrous potassium carbonate (3.4 g, 24.6 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (5:1) to give **26** as a white solid (4.2 g, yield 82.4%). M.p. 106–108 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.37 (s, 18 H, $-\text{CH}_3$), 4.70 (s, 2 H, $-\text{CH}_2\text{OH}$), 5.20 (s, 4 H, $-\text{OCH}_2-$), 6.57 (s, 1 H, Ph-H), 6.78 (s, 2 H, Ph-H), 7.50 [d, J = 8.1 Hz, 4 H, Ph-H (OXZ)], 7.55 [d, J = 7.8 Hz, 4 H, Ph-H (OXZ)], 8.05 [d, J = 8.0 Hz, 4 H, Ph-H (OXZ)], 8.15 [d, J = 7.8 Hz, 4 H, Ph-H (OXZ)] ppm.

(CZ)₂-(G-1)-CH₂Br (27): Triphenylphosphane (0.4 g, 1.5 mmol) was slowly added to a mixture of compound **25** (1.0 g, 1.72 mmol) and carbon tetrabromide (0.44 g, 1.25 mmol) in the minimum amount of anhydrous CH_2Cl_2 required to dissolve these reagents. After stirring under argon for 20 min, further carbon tetrabromide and triphenylphosphane were added in 1.25-equiv. amounts at 10-min intervals until TLC showed no starting benzyl alcohol anymore. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3×20 mL), and the combined extracts were dried with MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **27** as a pale-yellow solid (1.02 g, yield 92.1%). M.p. 163–164 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 4 H, $-\text{CH}_2-$), 2.10 (m, 4 H, $-\text{CH}_2-$), 3.85 (t, J = 6.1 Hz, 4 H, $-\text{OCH}_2-$), 4.20 (s, 2 H, $-\text{CH}_2\text{Br}$), 4.37 (t, J = 7.1 Hz, 4 H, $-\text{NCH}_2-$), 6.30 (s, 1 H, Ph-H), 6.45 (s, 2 H, Ph-H), 7.20 [t, J = 7.3 Hz, 4 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.8, J = 8.0 Hz, 8 H, Ph-H (CZ)], 8.20 [d, J = 7.8 Hz, 4 H, Ph-H (CZ)] ppm.

(OXZ)₂-(G-1)-CH₂Br (28): Triphenylphosphane (0.4 g, 1.5 mmol) was slowly added to a mixture of compound **26** (0.65 g, 0.90 mmol) and carbon tetrabromide (0.44 g, 1.25 mmol) in the minimum amount of anhydrous CH_2Cl_2 required to dissolve these reagents. After stirring under argon for 20 min, further carbon tetrabromide and triphenylphosphane were added in 1.25-equiv. amounts at 10-min intervals until TLC showed no starting benzyl alcohol anymore. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3×20 mL), the combined extracts were dried with MgSO_4 , and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (10:1) to give **28** as a pale-yellow solid (0.29 g, yield 41.3%). M.p. 97–98 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.38 (s, 18 H, $-\text{CH}_3$), 4.43 (s, 2 H, $-\text{CH}_2\text{Br}$), 5.14 (s, 4 H, $-\text{OCH}_2-$), 6.57 (s, 1 H, Ph-H), 6.68 (s, 2 H, Ph-H), 7.56 [d, J = 8.2 Hz, 4 H, Ph-H (OXZ)], 7.59 [d, J = 8.0 Hz, 4 H, Ph-H (OXZ)], 8.07 [d, J = 8.2 Hz, 4 H, Ph-H (OXZ)], 8.17 [d, J = 8.0 Hz, 4 H, Ph-H (OXZ)] ppm.

(CZ)₄-(G-2)-COOCH₃ (29): A mixture of compound **27** (1.4 g, 2.2 mmol), methyl 3,5-dihydroxybenzoate (0.17 g, 1.0 mmol), anhydrous potassium carbonate (1.2 g, 8.7 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure, the residue was partitioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The

combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (2:1) to give **29** as a white solid (1.2 g, yield 92.6%). M.p. 75–77 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 8 H, $-\text{CH}_2-$), 2.04 (m, 8 H, $-\text{CH}_2-$), 3.86 (s, 3 H, $-\text{OCH}_3$), 3.88 (m, 8 H, $-\text{OCH}_2-$), 4.35 (t, J = 6.7 Hz, 8 H, $-\text{NCH}_2-$), 4.90 (s, 4 H, $-\text{OCH}_2-$), 6.30 (s, 2 H, Ph-H), 6.50 (s, 4 H, Ph-H), 6.75 (s, 1 H, Ph-H), 7.20 [t, J = 7.1 Hz, 8 H, Ph-H (CZ)], 7.25 (s, 2 H, Ph-H), 7.30–7.50 [td, J = 7.5, J = 7.9 Hz, 16 H, Ph-H (CZ)], 8.10 [d, J = 7.6 Hz, 8 H, Ph-H (CZ)] ppm.

(OXZ)₄-(G-2)-COOCH₃ (30): A mixture of compound **28** (2.0 g, 2.6 mmol), methyl 3,5-dihydroxybenzoate (0.195 g, 1.2 mmol), anhydrous potassium carbonate (1.2 g, 8.7 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (10:1) to give **30** as a white solid (1.0 g, yield 54.8%). M.p. 111–113 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.37 (s, 36 H, $-\text{CH}_3$), 3.89 (s, 3 H, $-\text{OCH}_3$), 5.04 (s, 4 H, $-\text{OCH}_2-$), 5.14 (s, 8 H, $-\text{OCH}_2-$), 6.59 (s, 2 H, Ph-H), 6.70 (s, 4 H, Ph-H), 6.75 (s, 1 H, Ph-H), 7.20 (s, 2 H, Ph-H), 7.56 [m, 16 H, Ph-H (OXZ)], 8.05 [d, J = 8.2 Hz, 8 H, Ph-H (OXZ)], 8.14 [d, J = 8.1 Hz, 8 H, Ph-H (OXZ)] ppm.

(CZ)₄-(G-2)-COOH (31): A mixture of compound **29** (1.3 g, 1.0 mmol) and KOH (3.0 g, 53.6 mmol) in tetrahydrofuran/methanol (20 mL/40 mL) was refluxed with vigorous stirring for 30 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **31** as a white solid (1.1 g, yield 85.8%). The product was used directly in the next reaction without further purification. M.p. 94–96 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 8 H, $-\text{CH}_2-$), 2.06 (m, 8 H, $-\text{CH}_2-$), 3.90 (t, J = 6.0 Hz, 8 H, $-\text{OCH}_2-$), 4.40 (t, J = 6.7 Hz, 8 H, $-\text{NCH}_2-$), 4.92 (s, 4 H, $-\text{OCH}_2-$), 6.32 (s, 2 H, Ph-H), 6.50 (s, 4 H, Ph-H), 6.75 (s, 1 H, Ph-H), 7.20 [t, J = 7.1 Hz, 8 H, Ph-H (CZ)], 7.25 (s, 2 H, Ph-H), 7.30–7.50 [m, 16 H, Ph-H (CZ)], 8.12 [d, J = 7.6 Hz, 8 H, Ph-H (CZ)] ppm. MS (ESI): m/z = 1321.5 [M^+ + K].

(OXZ)₄-(G-2)-COOH (32): A mixture of compound **30** (1.0 g, 0.64 mmol) and KOH (1.0 g, 17.9 mmol) in tetrahydrofuran/methanol (40 mL/20 mL) was refluxed with vigorous stirring for 30 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **32** as a white solid (0.85 g, yield 85.8%). The product was used directly in the next reaction without further purification. M.p. 146–148 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.38 (s, 36 H, $-\text{CH}_3$), 5.05 (s, 4 H, $-\text{OCH}_2-$), 5.16 (s, 8 H, $-\text{OCH}_2-$), 6.59 (s, 2 H, Ph-H), 6.71 (s, 4 H, Ph-H), 6.75 (s, 1 H, Ph-H), 7.20 (s, 2 H, Ph-H), 7.58 [m, 16 H, Ph-H (OXZ)], 8.08 [d, J = 8.2 Hz, 8 H, Ph-H (OXZ)], 8.17 [d, J = 8.1 Hz, 8 H, Ph-H (OXZ)] ppm. MS (MALDI-TOF): m/z = 1559.2 [M^+].

(CZ)₄-(G-2)-CH₂OH (33): A mixture of compound **27** (8.3 g, 14.5 mmol), 3,5-dihydroxybenzyl alcohol (1.0 g, 7.1 mmol), anhydrous potassium carbonate (3.4 g, 24.6 mmol), and 18-crown-6

(0.38 g, 1.4 mmol) in anhydrous acetone (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure, the residue was partitioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×40 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **33** as a white solid (7.1 g, yield 79.2%). M.p. 96–98 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 8 H, $-\text{CH}_2-$), 2.05 (m, 8 H, $-\text{CH}_2-$), 3.85 (t, J = 6.1 Hz, 8 H, $-\text{OCH}_2-$), 4.37 (t, J = 7.0 Hz, 8 H, $-\text{NCH}_2-$), 4.62 (s, 2 H, $-\text{CH}_2\text{OH}$), 4.90 (s, 4 H, $-\text{OCH}_2-$), 6.25 (s, 2 H, Ph-H), 6.42 (s, 5 H, Ph-H), 6.50 (s, 2 H, Ph-H), 7.20 [t, J = 7.8 Hz, 8 H, Ph-H (CZ)], 7.40 [d, J = 7.9 Hz, 8 H, Ph-H (CZ)], 7.48 [t, J = 7.9 Hz, 8 H, Ph-H (CZ)], 8.20 [d, J = 7.7 Hz, 8 H, Ph-H (CZ)] ppm.

(CZ)₄-(G-2)-CH₂Br (34): Triphenylphosphane (1.2 g, 4.5 mmol) was slowly added to a mixture of compound **33** (4.0 g, 3.15 mmol) and carbon tetrabromide (1.5 g, 4.26 mmol) in the minimum amount of anhydrous CH_2Cl_2 required to dissolve these reagents. After stirring under argon for 20 min, further carbon tetrabromide and triphenylphosphane were added in 1.25-equiv. amounts at 10-min intervals until TLC showed no starting benzyl alcohol anymore. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3×20 mL), the combined extracts were dried with MgSO_4 , and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **34** as a pale-yellow solid (3.46 g, yield 82.4%). M.p. 64–65 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 8 H, $-\text{CH}_2-$), 2.07 (m, 8 H, $-\text{CH}_2-$), 3.88 (t, J = 6.1 Hz, 8 H, $-\text{OCH}_2-$), 4.36 (m, 10 H, $-\text{NCH}_2-$, $-\text{CH}_2\text{Br}$), 4.89 (s, 4 H, $-\text{OCH}_2-$), 6.30 (s, 2 H, Ph-H), 6.48 (s, 5 H, Ph-H), 6.60 (s, 2 H, Ph-H), 7.21 [t, J = 7.0 Hz, 8 H, Ph-H (CZ)], 7.40 [d, J = 8.1 Hz, 8 H, Ph-H (CZ)], 7.44 [t, J = 7.2 Hz, 8 H, Ph-H (CZ)], 8.10 [d, J = 7.7 Hz, 8 H, Ph-H (CZ)] ppm.

(CZ)₈-(G-3)-COOCH₃ (35): A mixture of compound **34** (3.0 g, 2.2 mmol), methyl 3,5-dihydroxybenzoate (0.17 g, 1.0 mmol), anhydrous potassium carbonate (1.2 g, 8.7 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure, the residue was partitioned between CH_2Cl_2 and H_2O , and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (2:1) to give **35** as a white solid (2.26 g, yield 84.7%). M.p. 76–78 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.75 (m, 16 H, $-\text{CH}_2-$), 2.00 (m, 16 H, $-\text{CH}_2-$), 3.62 (s, 3 H, $-\text{OCH}_3$), 3.85 (m, 16 H, $-\text{OCH}_2-$), 4.31 (t, J = 6.7 Hz, 16 H, $-\text{NCH}_2-$), 4.89 (s, 8 H, $-\text{OCH}_2-$), 4.93 (s, 4 H, $-\text{OCH}_2-$), 6.30–6.73 (19 H, Ph-H), 7.19 [m, 18 H, Ph-H, Ph-H (CZ)], 7.35–7.50 [td, J = 7.0, J = 8.0 Hz, 32 H, Ph-H (CZ)], 8.06 [d, J = 7.6 Hz, 16 H, Ph-H (CZ)] ppm. MS (MALDI-TOF): m/z = 2709.3 [M^+ + K].

(CZ)₈-(G-3)-COOH (36): A mixture of compound **35** (3.4 g, 1.3 mmol) and KOH (1.0 g, 17.9 mmol) in tetrahydrofuran/methanol (30 mL/30 mL) was refluxed with vigorous stirring for 30 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (400 mL). The precipitate was filtered off and washed with ethanol to give **36** as a white solid (2.7 g, yield 78.3%). The product was used directly in the next reaction

without further purification. M.p. 121–123 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.78 (m, 16 H, $-\text{CH}_2-$), 2.04 (m, 16 H, $-\text{CH}_2-$), 3.85 (m, 16 H, $-\text{OCH}_2-$), 4.31 (t, J = 6.7 Hz, 16 H, $-\text{NCH}_2-$), 4.85–4.95 (s, 12 H, $-\text{OCH}_2-$), 6.32–6.75 (m, 19 H, Ph-H), 7.19 [m, 18 H, Ph-H, Ph-H (CZ)], 7.35–7.50 [m, 32 H, Ph-H (CZ)], 8.06 [d, J = 7.6 Hz, 16 H, Ph-H (CZ)] ppm. MS (MALDI-TOF): m/z = 2695.3 [M^+ + K].

(CZ)₂-PTCDI-CH₂OH (38): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4,9,10-perylenebis(dicarboximide) (0.25 g, 0.28 mmol), compound **19** (0.17 g, 0.28 mmol), DCC (0.5 g, 2.4 mmol), and 4-(dimethylamino)pyridine (DMAP; 0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h. The mixture was then concentrated to dryness and the product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (20:1) to give **38** as a dark-red solid (16 mg, yield 3.9%). M.p. > 280 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.76 (m, 4 H, $-\text{CH}_2-$), 1.98 (m, 4 H, $-\text{CH}_2-$), 2.26 (s, 6 H, $-\text{CH}_3$), 2.31 (s, 6 H, $-\text{CH}_3$), 3.88 (t, J = 6.1 Hz, 4 H, $-\text{OCH}_2-$), 3.91 (t, J = 5.3 Hz, 2 H, HOCH_2-), 4.30 (t, J = 7.1 Hz, 4 H, $-\text{NCH}_2-$), 4.37 (m, 2 H, $-\text{NCH}_2-$), 4.56 (s, 4 H, $-\text{OCH}_2$, $-\text{NCH}_2-$), 6.50 (s, 1 H, Ph-H), 6.78 (d, J = 7.6 Hz, 8 H, Ph-H), 7.00 (d, J = 8.3 Hz, 4 H, Ph-H), 7.05 (d, J = 8.3 Hz, 4 H, Ph-H), 7.08 (s, 2 H, Ph-H), 7.18 [t, J = 7.3 Hz, 4 H, Ph-H (CZ)], 7.35–7.45 [td, J = 7.3, J = 8.1 Hz, 8 H, Ph-H (CZ)], 8.06 [d, J = 7.8 Hz, 4 H, Ph-H (CZ)], 8.09 (s, 2 H, perylene-H), 8.13 (s, 2 H, perylene-H) ppm.

(CZ)₁-(NP)₁-(G-1)-COOCH₃ (39): A mixture of *N*-(4-bromobutyl)-9*H*-carbazole (0.73 g, 2.4 mmol), *N*-(4-bromobutyl)-4-(piperidin-1-yl)-1,8-naphthalenedicarboximide (1.0 g, 2.4 mmol), methyl 3,5-dihydroxybenzoate (0.4 g, 2.4 mmol), anhydrous potassium carbonate (2.0 g, 14.5 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous THF (50 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated 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 (3 × 40 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (1:3) to give **39** as a yellow solid (0.57 g, yield 32.9%). M.p. 66–67 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.76–1.98 (m, 12 H, $-\text{CH}_2$), 2.12 (m, 2 H, $-\text{CH}_2$), 3.25 (s, 4 H, $-\text{NCH}_2$), 3.88 (s, 3 H, $-\text{OCH}_3$), 3.98 (t, J = 6.0 Hz, 2 H, $-\text{OCH}_2$), 4.02 (t, J = 5.1 Hz, 2 H, $-\text{OCH}_2$), 4.25 (t, J = 6.5 Hz, 2 H, $-\text{NCH}_2$), 4.38 (t, J = 7.0 Hz, 2 H, $-\text{NCH}_2$), 6.60 (s, 1 H, Ph-H), 7.10–7.20 (m, 3 H, Ph-H, naphthalene-H), 7.23 [t, J = 7.2 Hz, 2 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.6, J = 8.0 Hz, 4 H, Ph-H (CZ)], 7.68 (t, J = 8.0 Hz, 1 H, naphthalene-H), 8.10 [d, J = 7.7 Hz, 2 H, Ph-H (CZ)], 8.38 (d, J = 8.4 Hz, 1 H, naphthalene-H), 8.50 (d, J = 8.3 Hz, 1 H, naphthalene-H), 8.58 (d, J = 7.2 Hz, 1 H, naphthalene-H) ppm.

(CZ)₁-(NP)₁-(G-1)-COOH (40): A mixture of compound **39** (0.57 g, 0.8 mmol) and KOH (3.0 g, 53.6 mmol) in tetrahydrofuran/methanol (40 mL/20 mL) was refluxed with vigorous stirring for 20 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure and the residue was acidified with 10% aqueous HCl solution (300 mL). The precipitate was filtered off and washed with ethanol to give **40** as a yellow solid (0.45 g, yield 80.7%). The product was used directly in the next reaction without further purification. M.p. 110–111 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.76–2.12 (m, 14 H, $-\text{CH}_2$), 3.20 (s, 4 H, $-\text{NCH}_2$), 3.98 (t, J = 5.3 Hz, 2 H, $-\text{OCH}_2$), 4.02 (t, J = 5.1 Hz, 2 H, $-\text{OCH}_2$), 4.25 (t, J = 6.2 Hz, 2 H, $-\text{NCH}_2$), 4.39 (t, J = 6.8 Hz,

2 H, $-\text{NCH}_2$), 6.62 (s, 1 H, Ph-H), 7.12–7.20 (m, 3 H, Ph-H, naphthalene-H), 7.22 [t, J = 7.3 Hz, 2 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.5, J = 7.8 Hz, 4 H, Ph-H (CZ)], 7.68 (t, J = 7.9 Hz, 1 H, naphthalene-H), 8.10 [d, J = 7.7 Hz, 2 H, Ph-H (CZ)], 8.39 (d, J = 8.3 Hz, 1 H, naphthalene-H), 8.49 (d, J = 8.1 Hz, 1 H, naphthalene-H), 8.58 (d, J = 7.2 Hz, 1 H, naphthalene-H) ppm. MS (ESI): m/z = 732.3 [M^+ + Na].

(CZ)₁-(G-1)-OH (41): A mixture of 9-(4-bromobutyl)-9*H*-carbazole (2.0 g, 6.62 mmol), benzene-1,4-diol (3.5 g, 31.8 mmol), anhydrous potassium carbonate (1.0 g, 7.25 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (70 mL) was refluxed with vigorous stirring under argon for 36 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **41** as a white solid (1.31 g, yield 59.3%). M.p. 130–131 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.82 (m, 2 H, $-\text{CH}_2-$), 2.08 (m, 2 H, $-\text{CH}_2-$), 3.88 (t, J = 6.1 Hz, 2 H, $-\text{OCH}_2-$), 4.40 (m, 3 H, $-\text{NCH}_2-$, HO-Ph), 6.73 (s, 4 H, Ph-H), 7.23 [t, J = 7.0 Hz, 2 H, Ph-H (CZ)], 7.40–7.48 [td, J = 7.2, J = 8.1 Hz, 4 H, Ph-H (CZ)], 8.10 [d, J = 7.7 Hz, 2 H, Ph-H (CZ)] ppm.

(CZ)₂-(G-1)-OH (42): A mixture of benzene-1,4-diol (4.6 g, 41.8 mmol), compound **27** (2.7 g, 4.18 mmol), anhydrous potassium carbonate (0.65 g, 4.71 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (70 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **42** as a white solid (2.30 g, yield 81.6%). M.p. 151–152 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.82 (m, 4 H, $-\text{CH}_2-$), 2.07 (m, 4 H, $-\text{CH}_2-$), 3.91 (t, J = 6.1 Hz, 4 H, $-\text{OCH}_2-$), 4.39 (t, J = 7.1 Hz, 4 H, $-\text{NCH}_2-$), 4.89 (s, 2 H, $-\text{OCH}_2-$), 6.31 (s, 1 H, Ph-H), 6.51 (s, 2 H, Ph-H), 6.72 (d, J = 8.8 Hz, 2 H, Ph-H), 6.82 (d, J = 8.8 Hz, 2 H, Ph-H), 7.22 [t, J = 7.0 Hz, 4 H, Ph-H (CZ)], 7.40–7.48 [td, J = 7.3, J = 8.1 Hz, 8 H, Ph-H (CZ)], 8.10 [d, J = 7.6 Hz, 4 H, Ph-H (CZ)] ppm.

(CZ)₄-(G-2)-OH (43): A mixture of benzene-1,4-diol (5.0 g, 45.5 mmol), compound **34** (4.0 g, 3.0 mmol), anhydrous potassium carbonate (0.5 g, 3.62 mmol), and 18-crown-6 (0.4 g, 1.4 mmol) in anhydrous acetone (70 mL) was refluxed with vigorous stirring under argon for 60 h. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried with anhydrous MgSO_4 and the solvents evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **43** as a white solid (2.80 g, yield 68.6%). M.p. 61–63 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.80 (m, 8 H, $-\text{CH}_2-$), 2.05 (m, 8 H, $-\text{CH}_2-$), 3.88 (t, J = 6.0 Hz, 8 H, $-\text{OCH}_2-$), 4.32 (s, 1 H, HO-Ph), 4.37 (t, J = 7.0 Hz, 8 H, $-\text{NCH}_2-$), 4.88 (s, 2 H, $-\text{OCH}_2-$), 4.90 (s, 4 H, $-\text{OCH}_2-$), 6.30 (s, 2 H, Ph-H), 6.49 (s, 4 H, Ph-H), 6.51 (s, 1 H, Ph-H), 6.62 (s, 2 H, Ph-H), 6.67 (d, J = 8.9 Hz, 2 H, Ph-H), 6.76 (d, J = 8.9 Hz, 2 H, Ph-H), 7.21 [t, J = 7.1 Hz, 8 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.5, J = 8.0 Hz, 16 H, Ph-H (CZ)], 8.09 [d, J = 7.7 Hz, 8 H, Ph-H (CZ)] ppm.

Preparation of CZ- or OXZ-Terminated Imide-Type Dendrimers

2CZ-(G-1)-PTCDI (1): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.3 g, 0.33 mmol), compound **15** (0.48 g, 1.3 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (25 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness and the product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give dendrimer **1** as a dark-red solid (0.34 g, yield 64.2%). M.p. 136–137 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.85 (m, 4 H, $-\text{CH}_2-$), 2.10 (m, 4 H, $-\text{CH}_2-$), 2.30 (s, 12 H, $-\text{CH}_3$), 3.90 (t, J = 6.1 Hz, 4 H, $-\text{OCH}_2-$), 4.40 (t, J = 7.0 Hz, 4 H, $-\text{NCH}_2-$), 4.70 (s, 8 H, $-\text{OCH}_2-$, $-\text{NCH}_2-$), 6.75 (d, J = 7.0 Hz, 4 H, Ph-H), 6.80 (d, J = 8.4 Hz, 8 H, Ph-H), 7.06 (d, J = 8.4 Hz, 8 H, Ph-H), 7.20 [t, J = 7.7 Hz, 4 H, Ph-H (CZ)], 7.40–7.50 [td, J = 7.8, J = 8.2 Hz, 8 H, Ph-H (CZ)], 7.80 (d, J = 9.0 Hz, 4 H, Ph-H), 8.10 [d, J = 7.8 Hz, 4 H, Ph-H (CZ)], 8.12 (s, 4 H, perylene-H) ppm. MS (ESI): m/z = 1608.6 [M^+ + Na].

2OXZ-(G-1)-PTCDI (2): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.2 g, 0.22 mmol), compound **16** (0.4 g, 0.93 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (40 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (20:1) to give dendrimer **2** as a dark-red solid (0.21 g, yield 55.4%). M.p. 153–155 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.38 (s, 18 H, $-\text{CH}_3$), 2.30 (s, 12 H, $-\text{CH}_3$), 4.55 (s, 8 H, $-\text{CH}_2-$), 5.15 (s, 4 H, $-\text{OCH}_2-$), 6.85 (d, J = 8.4 Hz, 8 H, Ph-H), 6.91 (d, J = 8.4 Hz, 4 H, Ph-H), 7.08 (d, J = 8.3 Hz, 8 H, Ph-H), 7.58 [t, J = 8.6 Hz, 8 H, Ph-H (OXZ)], 7.90 (d, J = 8.7 Hz, 4 H, Ph-H), 8.07 [d, J = 8.4 Hz, 4 H, Ph-H (OXZ)], 8.16 [m, 8 H, perylene-H, Ph-H (OXZ)] ppm. MS (ESI): m/z = 1746.3 [M^+ + Na].

4CZ-(G-1)-PTCDI (3): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.2 g, 0.22 mmol), compound **19** (0.5 g, 0.84 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give dendrimer **3** as a dark-red solid (0.24 g, yield 52.5%). M.p. 230–233 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.65 (m, 8 H, $-\text{CH}_2-$), 1.90 (m, 8 H, $-\text{CH}_2-$), 2.15 (s, 12 H, $-\text{CH}_3$), 3.80 (t, J = 6.1 Hz, 8 H, $-\text{OCH}_2-$), 4.20 (t, J = 7.1 Hz, 8 H, $-\text{NCH}_2-$), 4.48 (s, 8 H, $-\text{OCH}_2-$, $-\text{NCH}_2-$), 6.40 (s, 2 H, Ph-H), 6.64 (d, J = 8.4 Hz, 8 H, Ph-H), 6.88 (d, J = 8.4 Hz, 8 H, Ph-H), 7.05 (s, 4 H, Ph-H), 7.10 [t, J = 7.6 Hz, 8 H, Ph-H (CZ)], 7.25–7.35 [td, J = 7.4, J = 8.0 Hz, 16 H, Ph-H (CZ)], 7.95 [d, J = 7.7 Hz, 8 H, Ph-H (CZ)], 8.05 (s, 4 H, perylene-H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.96, 25.92, 26.98, 39.40, 42.82, 62.66, 67.88, 107.31, 107.82, 108.80, 119.03, 119.56, 119.98, 120.57, 120.61, 120.61, 122.40, 123.02, 125.85, 130.69, 131.92, 132.98, 134.42, 140.48, 153.15, 156.25, 159.98, 163.56, 166.31 ppm. MS (MALDI-TOF): m/z = 2058.9 [M^+ + 1].

4OXZ-(G-1)-PTCDI (4): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.25 g, 0.28 mmol), compound **20** (0.8 g, 1.1 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (20:1) to give dendrimer **4** as a dark-red solid (0.29 g, yield 44.3%). M.p. 179–180 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.38 (s, 36 H, $-\text{CH}_3$), 2.25 (s, 12 H, $-\text{CH}_3$), 4.55 (s, 8 H, $-\text{CH}_2-$), 5.03 (s, 8 H, $-\text{OCH}_2-$), 6.76 (m, 10 H, Ph-H), 7.02 (d, J = 8.3 Hz, 8 H, Ph-H), 7.21 (s, 4 H, Ph-H), 7.50 [d, J = 8.2 Hz, 8 H, Ph-H (OXZ)], 7.55 [d, J = 8.4 Hz, 8 H, Ph-H (OXZ)], 8.05 [m, 16 H, Ph-H (OXZ)], 8.13 (s, 4 H, perylene-H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.99, 31.35, 34.16, 35.34, 69.56, 108.47, 119.54, 119.93, 120.08, 120.56, 121.19, 122.43, 123.75, 126.31, 127.00, 127.27, 128.02, 130.74, 132.23, 133.01, 134.56, 140.44, 153.08, 155.64, 156.41, 159.55, 163.56, 164.27, 164.92, 166.00 ppm. MS (MALDI-TOF): m/z = 2357.9 [M^+ + Na].

6CZ-(G-1)-PTCDI (5): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.2 g, 0.22 mmol), compound **23** (0.6 g, 0.72 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (200:1) to give dendrimer **5** as a dark-red solid (0.27 g, yield 49.3%). M.p. 120–122 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.53 (m, 4 H, $-\text{CH}_2-$), 1.65 (m, 8 H, $-\text{CH}_2-$), 1.85 (m, 12 H, $-\text{CH}_2-$), 2.20 (s, 12 H, $-\text{CH}_3$), 3.80 (m, 12 H, $-\text{OCH}_2-$), 4.05 (t, J = 7.2 Hz, 4 H, $-\text{NCH}_2-$), 4.15 (t, J = 7.1 Hz, 8 H, $-\text{NCH}_2-$), 4.51 (s, 8 H, $-\text{OCH}_2-$, $-\text{NCH}_2-$), 6.67 (d, J = 8.4 Hz, 8 H, Ph-H), 6.90 (d, J = 8.3 Hz, 8 H, Ph-H), 7.10–7.20 [m, 20 H, Ph-H, Ph-H (CZ)], 7.25 [m, 8 H, Ph-H (CZ)], 7.33 [t, J = 7.5 Hz, 12 H, Ph-H (CZ)], 8.0–8.05 [m, 12 H, Ph-H (CZ)], 8.10 (s, 4 H, perylene-H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 20.62, 25.61, 26.80, 27.74, 39.23, 42.42, 42.53, 62.54, 68.39, 72.66, 108.00, 108.53, 108.67, 118.75, 118.79, 119.32, 119.68, 120.29, 120.35, 122.21, 122.79, 124.67, 125.53, 125.56, 130.42, 132.77, 134.18, 140.24, 140.29, 141.68, 152.29, 152.88, 156.01, 163.28, 165.94 ppm. MS (MALDI-TOF): m/z = 2558.3 [M^+ + Na].

6OXZ-(G-1)-PTCDI (6): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.3 g, 0.33 mmol), compound **24** (1.0 g, 0.96 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (50 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (20:1) to give dendrimer **6** as a dark-red solid (0.36 g, yield 37.0%). M.p. 191–193 °C. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 1.36 (s, 54 H, $-\text{CH}_3$), 2.25 (s, 12 H, $-\text{CH}_3$), 4.50 (s, 8 H, $-\text{CH}_2-$), 5.00 (s, 8 H, $-\text{OCH}_2-$), 5.20 (s, 4 H, $-\text{OCH}_2-$), 6.75 (d, J = 8.3 Hz, 8 H, Ph-H), 7.00 (d, J = 8.4 Hz, 8 H, Ph-H), 7.32 (s, 4 H, Ph-H), 7.45–7.55 [m, 24 H, Ph-H (OXZ)], 8.00 [m, 24 H, Ph-H (OXZ)], 8.10 (s, 4 H, perylene-H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 21.36, 31.76, 35.72, 39.75, 63.05, 70.86, 75.29, 109.57, 120.29, 120.47, 120.98, 121.63, 122.90, 124.24, 124.30, 126.68, 127.39, 127.42, 127.62, 128.51, 129.17, 131.16, 135.02, 140.78, 141.88, 152.72, 153.48,

155.92, 155.99, 156.85, 163.95, 164.62, 164.76, 165.34 ppm. MS (MALDI-TOF): m/z = 2950.0 [M^+].

8CZ-(G-2)-PTCDI (7): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.2 g, 0.22 mmol), compound **31** (0.8 g, 0.62 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give dendrimer **7** as a violet-red solid (0.19 g, yield 25.2%). M.p. 115–117 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.70 (m, 16 H, $-CH_2-$), 2.00 (m, 16 H, $-CH_2-$), 2.18 (s, 12 H, $-CH_3$), 3.80 (tt, J = 6.1, J = 6.1 Hz, 16 H, $-OCH_2-$), 4.30 (tt, J = 7.1, J = 7.0 Hz, 16 H, $-NCH_2-$), 4.44 (s, 4 H, $-CH_2-$), 4.45 (s, 4 H, $-CH_2-$), 4.80 (s, 8 H, $-OCH_2-$, $-NCH_2-$), 6.20 (s, 4 H, Ph-H), 6.40 (s, 8 H, Ph-H), 6.65 (s, 2 H, Ph-H), 6.72 (d, J = 8.4 Hz, 8 H, Ph-H), 6.90 (d, J = 8.4 Hz, 8 H, Ph-H), 7.18 [m, 20 H, Ph-H, Ph-H (CZ)], 7.30–7.40 [m, 32 H, Ph-H (CZ)], 8.05 [m, 20 H, Ph-H (CZ), perylene-H] ppm. MS (MALDI-TOF): m/z = 3457.4 [M^+ + Na].

8OXZ-(G-2)-PTCDI (8): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.2 g, 0.22 mmol), compound **32** (2.0 g, 1.28 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (40 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2/CH_3COCH_3 (10:1) to give dendrimer **8** as a dark-red solid (0.12 g, yield 13.7%). M.p. 156–158 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.35 (s, 72 H, $-CH_3$), 2.21 (s, 12 H, $-CH_3$), 4.55 (s, 8 H, $-CH_2-$), 4.98 (s, 24 H, $-OCH_2-$), 6.42 (s, 4 H, Ph-H), 6.50–6.8 (m, 26 H, Ph-H), 7.11 (s, 4 H, Ph-H), 7.55 [m, 32 H, Ph-H (OXZ)], 8.00–8.10 [m, 36 H, Ph-H (OXZ), perylene-H] ppm. MS (MALDI-TOF): m/z = 3972.4 [M^+].

2CZ-2OXZ-(G-1)-PTCDI (9): A mixture of **38** (0.034 g, 0.023 mmol), **20** (0.10 g, 0.14 mmol), DCC (0.25 g, 1.2 mmol), and DMAP (0.1 g, 0.8 mmol) in anhydrous CH_2Cl_2 (20 mL) was stirred at room temperature for 24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2/CH_3COCH_3 (20:1) to give **9** as a dark-red solid (8 mg, yield 15.8%). M.p. 142–143 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.36 (s, 18 H, $-CH_3$), 1.75 (m, 4 H, $-CH_2-$), 1.95 (m, 4 H, $-CH_2-$), 2.25 (2 $\times$ s, 12 H, $-CH_3$), 3.87 (t, J = 6.0 Hz, 4 H, $-OCH_2-$), 4.30 (t, J = 6.0 Hz, 4 H, $-NCH_2-$), 4.57 (s, 8 H, $-CH_2-$), 5.05 (s, 4 H, $-OCH_2-$), 6.50 (s, 1 H, Ph-H), 6.75 (m, 8 H, Ph-H), 6.80 (s, 1 H, Ph-H), 6.97 (m, 8 H, Ph-H), 7.10 (s, 2 H, Ph-H), 7.15 [t, J = 7.3 Hz, 4 H, Ph-H (CZ)], 7.20 (s, 2 H, Ph-H), 7.35–7.45 [td, J = 7.0, J = 8.1 Hz, 8 H, Ph-H (CZ)], 7.48 [d, J = 7.7 Hz, 4 H, Ph-H (OXZ)], 7.55 [d, J = 8.5 Hz, 4 H, Ph-H (OXZ)], 8.05 [m, 12 H, Ph-H (OXZ), Ph-H (CZ)], 8.10 (2 $\times$ s, 4 H, perylene-H) ppm. MS (MALDI-TOF): m/z = 2197.9 [M^+].

Preparation of Cascade Energy-Transfer Imide-Type Dendrimers

2CZ-2NP-(G-1)-PTCDI (10): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.1 g, 0.11 mmol), compound **40** (0.2 g, 0.28 mmol), DCC (0.5 g, 2.4 mmol), and DMAP (0.2 g, 1.6 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred at room temperature for

24 h. During this time more DCC and DMAP were added, as required, until TLC showed no remaining starting materials. The mixture was then concentrated to dryness. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2/CH_3COCH_3 (200:1) to give **10** as a dark-red solid (75 mg, yield 29.9%). M.p. 139–140 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.70–1.88 (m, 24 H, $-CH_2-$), 1.97 (m, 4 H, $-CH_2-$), 2.25 (s, 12 H, $-CH_3$), 3.20 (s, 8 H, $-NCH_2-$), 3.87 (m, 8 H, $-OCH_2-$), 4.13 (s, 4 H, $-NCH_2-$), 4.30 (t, J = 7.1 Hz, 4 H, $-NCH_2-$), 4.52 (s, 8 H, $-CH_2-$), 6.52 (s, 2 H, Ph-H), 6.75 (d, J = 8.4 Hz, 8 H, Ph-H), 7.00 (d, J = 8.4 Hz, 8 H, Ph-H), 7.08 (s, 4 H, Ph-H), 7.12 (d, J = 8.1 Hz, 2 H, naphthalene-H), 7.18 [t, J = 7.5 Hz, 4 H, Ph-H (CZ)], 7.35–7.45 [td, J = 7.6, J = 8.1 Hz, 8 H, Ph-H (CZ)], 7.63 (t, J = 8.2 Hz, 2 H, naphthalene-H), 8.05 [m, 8 H, perylene-H, Ph-H (CZ)], 8.32 (d, J = 8.0 Hz, 2 H, naphthalene-H), 8.38 (d, J = 8.2 Hz, 2 H, naphthalene-H), 8.50 (d, J = 7.3 Hz, 2 H, naphthalene-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.35, 24.96, 25.35, 26.30, 26.84, 27.39, 39.79, 40.34, 43.24, 55.13, 62.86, 68.26, 68.41, 108.25, 108.32, 109.21, 115.25, 119.40, 120.32, 120.46, 120.90, 121.00, 122.76, 123.43, 123.65, 125.93, 126.24, 130.44, 131.08, 131.55, 132.25, 133.21, 134.78, 140.91, 153.60, 156.69, 157.81, 160.32, 160.54, 163.90, 164.59, 165.09, 166.72 ppm. MS (MALDI-TOF): m/z = 2286.1 [M^+].

Preparation of CZ-Terminated Bay-Type Dendrimers

4CZ-(G-1)-PTCDI (11): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.85 g, 1.0 mmol), compound **41** (1.65 g, 5.0 mmol), and anhydrous potassium carbonate (6.7 g, 48.6 mmol) in anhydrous DMF (40 mL) was stirred vigorously at 140 °C under argon for 24 h. After cooling to room temperature, the mixture was added to H_2O (200 mL). The precipitate was filtered off and dried. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **11** as a dark-red solid (0.34 g, yield 16.8%). M.p. 154–156 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.12 (d, J = 6.6 Hz, 24 H, $-CH_3$), 1.77 (m, 8 H, $-CH_2-$), 2.04 (m, 8 H, $-CH_2-$), 2.68 (m, 4 H, $-CH-$), 3.83 (t, J = 6.0 Hz, 8 H, $-OCH_2-$), 4.37 (t, J = 7.0 Hz, 8 H, $-NCH_2-$), 6.74 (d, J = 9.0 Hz, 8 H, Ph-H), 6.89 (d, J = 8.9 Hz, 8 H, Ph-H), 7.23 [t, J = 7.4 Hz, 8 H, Ph-H (CZ)], 7.27 (s, 4 H, Ph-H), 7.28 (s, 2 H, Ph-H), 7.38–7.48 [td, J = 7.4, J = 8.2 Hz, 16 H, Ph-H (CZ)], 8.09 [d, J = 7.8 Hz, 8 H, Ph-H (CZ)], 8.16 (s, 4 H, perylene-H) ppm. MS (MALDI-TOF): m/z = 2028.3 [M^+].

8CZ-(G-2)-PTCDI (12): A mixture of *N,N'*-bis(2-hydroxyethyl)-1,6,7,12-tetrakis(4-methylphenoxy)-3,4:9,10-perylenebis(dicarboximide) (0.53 g, 0.63 mmol), compound **42** (2.3 g, 3.4 mmol), and anhydrous potassium carbonate (1.5 g, 10.9 mmol) in anhydrous DMF (40 mL) was stirred vigorously at 140 °C under argon for 24 h. After cooling to room temperature, the mixture was added to H_2O (200 mL). The precipitate was filtered off and dried. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **12** as a dark-red solid (0.45 g, yield 21.0%). M.p. 104–106 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.12 (d, J = 6.2 Hz, 24 H, $-CH_3$), 1.78 (m, 16 H, $-CH_2-$), 2.03 (m, 16 H, $-CH_2-$), 2.70 (m, 4 H, $-CH-$), 3.87 (t, J = 6.0 Hz, 16 H, $-OCH_2-$), 4.33 (t, J = 7.0 Hz, 16 H, $-NCH_2-$), 4.89 (s, 8 H, $-OCH_2-$), 6.31 (s, 4 H, Ph-H), 6.51 (s, 8 H, Ph-H), 6.88 (d, J = 9.0 Hz, 8 H, Ph-H), 6.94 (d, J = 9.0 Hz, 8 H, Ph-H), 7.21 [t, J = 7.3 Hz, 16 H, Ph-H (CZ)], 7.27 (s, 4 H, Ph-H), 7.28 (s, 2 H, Ph-H), 7.38–7.48 [td, J = 7.5, J = 8.1 Hz, 32 H, Ph-H (CZ)], 8.08 [d, J = 7.7 Hz, 16 H, Ph-H (CZ)], 8.18 (s, 4 H, perylene-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.76, 26.51, 27.62, 29.80, 43.34, 68.26, 71.23, 101.63, 106.56, 109.36, 116.93, 119.54, 120.11, 120.67, 120.94, 121.06,

122.09, 123.43, 123.56, 124.57, 126.35, 139.86, 141.06, 146.38, 149.46, 156.59, 157.30, 160.98, 164.01 ppm. MS (MALDI-TOF): $m/z = 3425.4$ [$M^+ + Na$].

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