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# Synthesis and Characterization of Carbazole-Based Dendrimers with Porphyrin Cores

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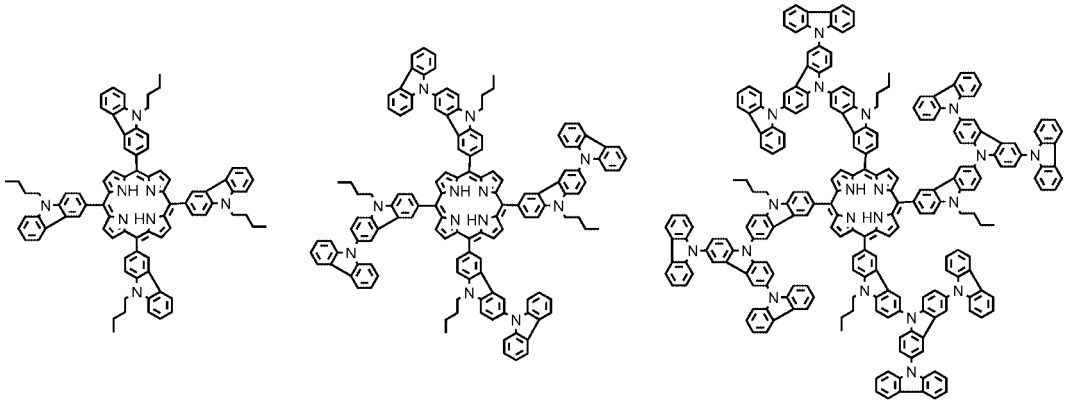
A series of novel dendritic carbazole-based porphyrins [T(Cz-G*n*)Ps] have been synthesized by a combination of Ullmann coupling and Adler condensation reactions and their intramolecular energy-transfer properties have been studied by absorption and steady-state fluorescence spectroscopy. It has been found that the light-harvesting capabilities of T(Cz-G*n*)Ps increase with increasing generation, but that the efficiency of the energy transfer decreases from T(Cz-G0)P to T(Cz-G2)P due to the Förster energy-transfer process. In addition, these dendritic macromolecules can emit intense red light with high fluorescence quantum yields and so may find applications in photonic devices.


## Introduction

Dendrimers are monodisperse, highly branched macromolecules with well defined three-dimensional structures, based on an interior core with a regular array of branching units.[1] Increasing attention has recently been focused on the incorporation of functional units into such dendritic structures to provide new nanoscopic materials with desirable properties.[2,3] To encapsulate a porphyrin core in the interior of a dendritic structure with various dendron units is an interesting undertaking that may find many attractive applications, since porphyrins are excellent functional organic molecules, and their functionalities are often affected by the local environment.[3] Of particular interest is their efficient light-harvesting ability for use as antennas. Although considerable efforts in the exploration of light-harvesting dendritic porphyrins with flexible[3b,3f,3m,3n] and rigid[3c–3e,3g,3h,3k,3l,3o] dendrons have already been made, the development of π-conjugated porphyrin-containing dendrimers is still the subject of much attention. On the other hand, carbazole is a promising building block for dendritic construction because of its chemical structure and special electronic and optical properties.[2i,2k,4] Construction of a rigid carbazole dendron around a porphyrin core may result in interesting photochemical, electrochemical, and catalytic properties, but there has so far been no example of a por-




Scheme 1. Molecular structures of T(Cz-G*n*)Ps.

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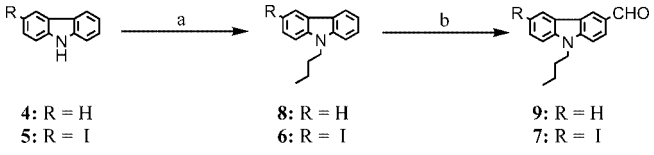
phyrin directly covalently linked to a carbazole dendron. Here we report the synthesis, characterization, and photophysical behaviors of porphyrins with four monodisperse dendritic carbazole arms (Scheme 1). We have found that the light-harvesting abilities of T(Cz-G*n*)Ps increase with increasing generation. Meanwhile, the carbazole-based dendrimers can emit intense red light with high fluorescence quantum yields, because the carbazole units can reduce the self-quenching of the fluorescence of the porphyrin cores, and they may be good candidates for photonic devices.

## Results and Discussion

### Synthesis of the Carbazole-Based Dendrons

The synthetic routes to the carbazole dendrons **9**, **11**, and **13** are shown in Schemes 2 and 3. Firstly, iodination of carbazole with $KI/KIO_3$ in AcOH at 80 °C provided compound **5** in a yield of 56%.[5] *N*-Alkylation of compounds **4** and **5** with 1-bromobutane was carried out at 0 °C in DMF containing NaH, giving compounds **6** and **8**, respectively, in quantitative yields.[6] 9-Butylcarbazole-3-carbaldehyde (**9**) was readily obtained from **8** through a Vilsmeier reaction in a yield of 79%,[7] and compound **7**, an important intermediate for the synthesis of larger carbazole dendrons, was prepared from **6**, also through a Vilsmeier reaction.



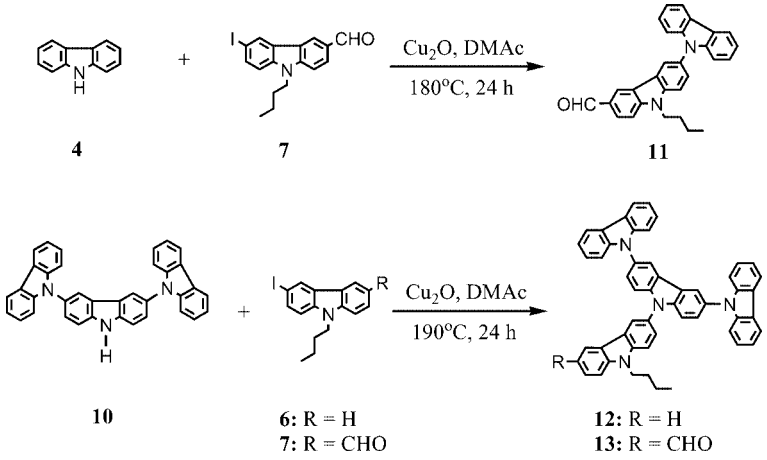

Scheme 2. Synthesis of compounds **7** and **9**. Reagents and conditions: a) (i) NaH, DMF, 20 min, (ii) *n*-$C_4H_9Br$, room temp., 1 h. b) $POCl_3$, DMF, $ClCH_2CH_2Cl$, reflux, 8 h.

Compounds **11** and **13** were synthesized by Ullmann coupling of **7** with compounds **4** and **10**, respectively (Scheme 3).[2i,2k,4d,4e,8] Compound **10** was synthesized as described in the literature,[2i,2k] with the reaction being carried out in *N*,*N*-dimethylacetamide (DMAc), with $Cu_2O$ catalysis at 160 °C. The reactivities of the N–H groups in the carbazole moieties in the Ullmann reaction decreased with increasing generation of the dendron, so compound **13** was obtained from compounds **7** and **10** at 180 °C. Although the Ullmann coupling conditions were harsh, the aldehyde groups in the obtained carbazole dendrons did not decompose. The pure carbazole dendrons could be readily recrystallized from THF/EtOH in moderate yields. Because the Ullmann coupling reactions were catalyzed by $Cu_2O$, and the residual $Cu^{2+}$ present would coordinate with porphyrin in the later Adler reaction, the obtained aldehydes **11** and **13** were further purified by column chromatography. In order to study the photoinduced energy interactions between carbazole units and phorphyrin cores in the dendrimers conveniently, the carbazole dendron **12** was also synthesized in an Ullmann coupling reaction.

### Synthesis of the Dendrimers

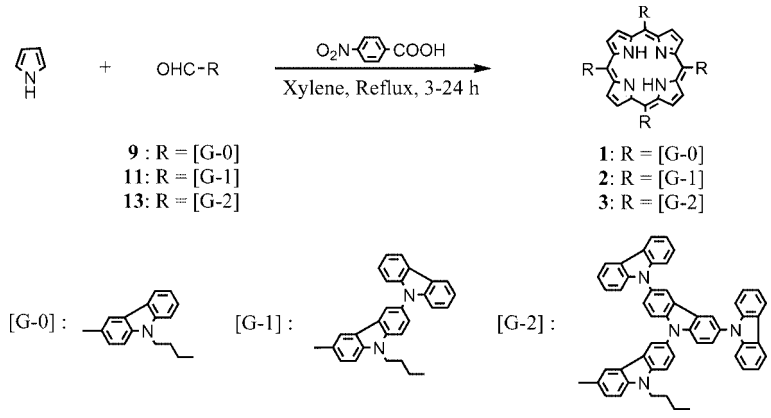
The synthesis of dendritic carbazole-based porphyrins is shown in Scheme 4.[9] The obtained aldehydes **9**, **11**, and **13** were converted into the corresponding dendritic porphyrins T(Cz-G*n*)Ps (**1**–**3**) under Adler conditions in xylene and in the presence of 4-nitrobenzoic acid as the catalyst in yields of 21%, 11%, and 7%, respectively. It was found that the Adler condensation time increased with the increase in the carbazole dendrons' volumes: the formation of T(Cz-G0)P, for instance, needed 3 h, whilst T(Cz-G1)P and T(Cz-G2)P were synthesized over 10 h and 24 h, respectively. According to previous reports the conditions of the Adler condensation are harsh and the yields low, but the reaction was easy to operate and gave moderate yields. We also adopted Lindsey conditions to prepare the above porphyrins, but only traces of T(Cz-G*n*)Ps were obtained when trifluoroacetic acid was used as catalyst in $CH_2Cl_2$ in the dark, following by DDQ oxidation and $Et_3N$ neutralization.[10]

The obtained dendritic porphyrins T(Cz-G*n*)Ps were soluble in chloroform, THF, and $CH_2Cl_2$, their solubilities increasing with the generation. All intermediates and final




Scheme 3. Synthesis of carbazole dendrons **11**, **12**, and **13**.




Scheme 4. Synthesis of T(Cz-G*n*)Ps.

products were purified by column chromatography on silica gel and characterized by FT-IR and $^1$H NMR spectroscopy, MALDI-TOF mass spectrometry, and GPC. The MALDI-TOF mass spectra of T(Cz-G*n*)Ps **1**–**3** are given in the Supporting Information, and the results fitted the calculated values very well. The gel permeation chromatography (GPC) eluting curves of **1**–**3** each showed a symmetrical, narrow peak, which indicated high purity (see Figures S1–S3, Supporting Information).

### Optical Properties of T(Cz-G*n*)Ps

The absorption and fluorescent emission data for T(Cz-G*n*)Ps **1**, **2**, and **3** are listed in Table 1. In THF, we can observe several absorption bands in the visible region, including four Q-bands in the 500–700 nm region (consistent with a free-base porphyrin), together with the Soret band at ca. 430 nm, and others in the UV region (250–350 nm) due to carbazole units (see Figure 1). With increasing generation number the molar extinction coefficients of the porphyrin units remained constant, but those for the carbazole dendrons in the UV region increased because of the growing numbers of carbazole units, whereas no spectral broadening or spectral shift took place. This suggested that the electronic structures of the dendritic porphyrins were not changing with increasing generation number, which provided an opportunity to excite the dendrons selectively and to study the intramolecular energy transfer properties.[2a,3b] As can be seen in Figure 2, we found that the Soret band of TPP + **12** appeared at the same region as that of TPP, which meant that physical mixing of the carbazole dendron with TPP could not induce a shift in the Soret band. However, the Soret band of **3** was red-shifted by 16 nm relative to TPP, which indicated that the carbazole in compound **3** was partially conjugated with the porphyrin ring. As shown in Figure 3, the absorption bands for the porphyrin cores of compounds **1**–**3** in films were bathochromically shifted in relation to those in solution, due to the aggregation effect, with the degree of redshift depending on the generation number of the dendrimer: the absorptions of **1**, **2**, and **3** in films, for example, were red-shifted by 19, 18, and 15 nm, respectively, or in other words, the higher the generation, the smaller the redshift in the absorption. We deduced that the dendrons in higher-generation dendrimers had a site isolation effect on the porphyrin core.

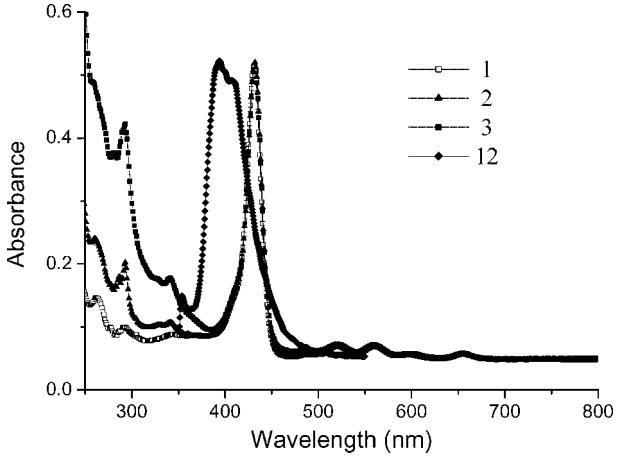



Figure 1. UV/Vis absorption spectra of **1**–**3** in THF (1 μM). The dotted curve represents the fluorescence spectrum of the dendron **12** in THF (1 μM) upon excitation at 293 nm.

Table 1. Absorption and fluorescence emission data in THF and in thin film for T(Cz-G*n*)Ps.

| Dendrimer | In THF | | | | $\Phi_{ET}$[b] | In film | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\lambda^{abs}_{max}$ [nm] | | $\lambda^{em}_{max}$[a] [nm] | | | $\lambda^{abs}_{max}$ [nm] | | $\lambda^{em}_{max}$[c] [nm] | |
| T(Cz-G0)P | 293, 342 | 431 | 347 | 665, 725 | 69% | 295, 348 | 450 | 678 | 747 |
| T(Cz-G1)P | 293, 342 | 432 | 384 | 666, 727 | 65% | 297, 347 | 450 | 671 | 730 |
| T(Cz-G2)P | 292, 341 | 431 | 392 | 664, 730 | 40% | 298, 343 | 446 | 671 | 732 |

[a] Excited at 293 nm. [b] Energy transfer efficiency ($\Phi_{ET}$) was calculated by comparison of the absorption and excitation spectra of dendrimers with monitoring of the emission of the porphyrin core (664 nm) in THF. [c] Excited at 451 nm.

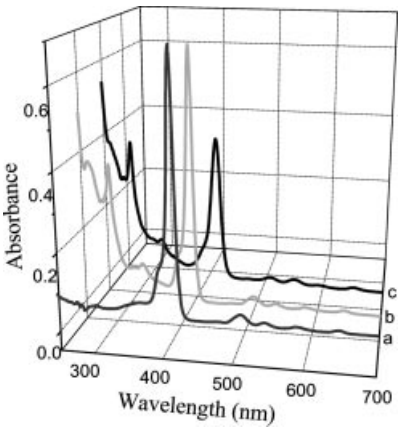



Figure 2. UV/Vis absorption spectra of (a) TPP, (b) TPP + **12** (TPP mixed with 4 equiv. of **12**), and (c) compound **3** in THF (1 μM).

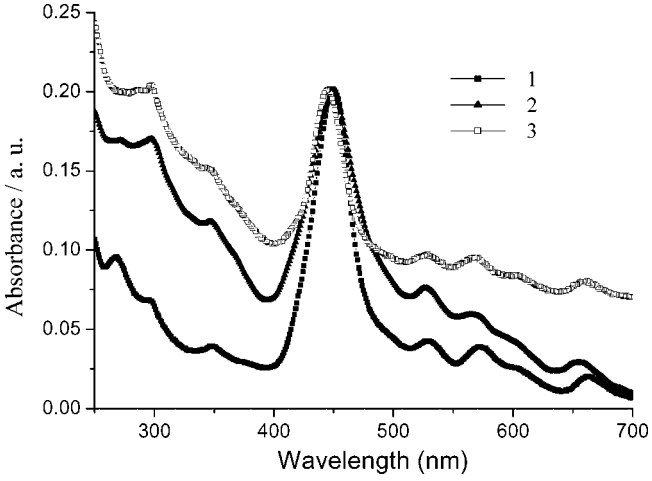



Figure 3. Normalized absorption spectra of **1**–**3** (film).

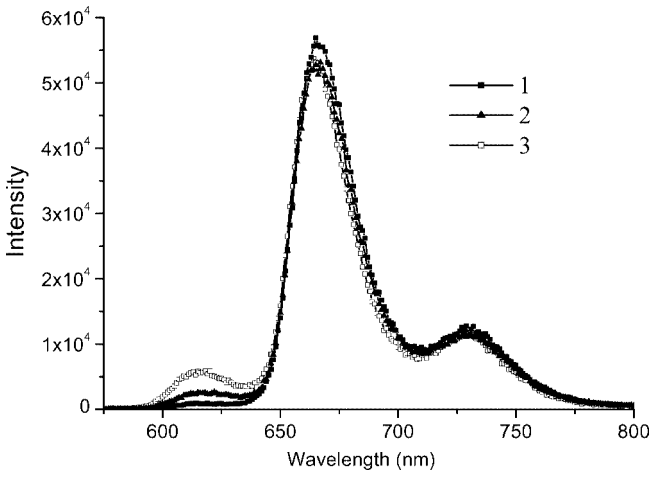



Figure 4. Emission spectra of **1**–**3** at 1 μM in THF ($\lambda_{ex}$ = 432 nm).

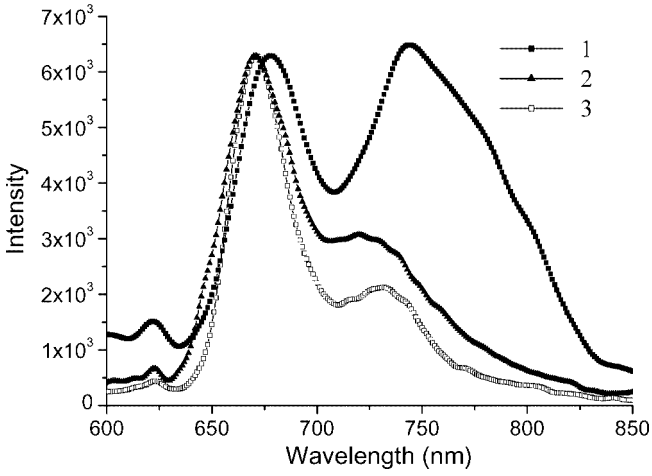



Figure 5. Normalized fluorescence spectra of **1**–**3** (film) excited at 451 nm.

As can be seen in Figure 4, we were able to find that, in THF, all dendrimers showed characteristic luminescence of their porphyrin cores, with two emission bands at ca. 664 nm and 730 nm on excitation at 432 nm. In films, the emission bands located at around 670 nm were broadened and red-shifted – relative to the fluorescence in solution – by 14, 6, and 6 nm for T(Cz-G0)P, T(Cz-G1)P, and T(Cz-G2)P, respectively (as shown in Figure 5). The results indicated that the higher-generation dendrimer had a smaller Stokes shift than the lower one, indicative to a certain extent of a site isolation or dendron dilution effect, reducing the extent or possibility of aggregation of the core. However, the attachment of the above dendrons to the porphyrin could not completely shield the chromophore core.

Bifunctional dendrimers represented an ideal architecture with which to reveal the interaction between chromophores. On excitation at 293 nm, compound **12** emitted strong fluorescence at 394 nm, partially overlapping with the Soret band of the porphyrin core (see Figure 1). A singlet–singlet Förster energy transfer might therefore take place in T(Cz-G*n*)Ps, as was clearly demonstrated by the excitation and absorption spectra (see Figure 6). These showed that porphyrins connected to peripheral carbazole units could have light-harvesting potential, and that it was possible to obtain intense emission from the core when excited by sensitization from the large light-harvesting antenna. As discussed above, we were able to address the carbazole dendrons and the porphyrin core independently by changing the excitation wavelength because of the following facts: (1) the absorption spectra of the two chromophores did not overlap, and (2) the carbazole dendron functionalized porphyrin could not significantly perturb the electronic transition in the ground state. As shown in Figure 7, on excitation at 293 nm T(Cz-G*n*)Ps gave strong emission bands at 664 nm and 730 nm attributable to the emission of porphyrin cores and weak emissions due to carbazole dendrons. Because the porphyrin should not emit red light under excitation at 293 nm, we concluded that intramolecular energy transfer from carbazole units to porphyrin cores (energy trap) was taking place. It was also found that the red photoluminescence was enhanced with increasing generation, which suggested that the light-harvesting abilities improved from **1** to **3** because of the multiplying of the number of carbazole units (energy-collecting sites). A mix-

ture of TPP and **12** showed no porphyrin moiety emission bands when excited at 293 nm; thus, as expected, no energy transfer took place between compound **12** and TPP in a simple mixture, but the carbazole units in the dendrimers exhibited significant light-harvesting for the luminescence of porphyrin cores. The efficiency of energy transfer ($\Phi_{ET}$) could be estimated by comparing the UV/Vis spectrum with the excitation spectrum recorded at 293 nm,[2a,3b,11] and the $\Phi_{ET}$ values for T(Cz-G*n*)Ps (**1**–**3**) were found to be 69%, 65%, and 40%, respectively (see Figure 6). It was clear that the energy-transfer efficiency decreased for the higher-generation dendrimers, which could be explained by the Förster mechanism of energy transfer, and that the distance between the donor and the acceptor might play an important role in the $\Phi_{ET}$.[2a] These results were similar to the findings of W. Dehaen et al., but the energy transfer did not reach 100% in our system.[3o] In addition, on direct excitation of the core, the Förster energy transfer between the periphery donors and the core acceptor in the dendrimers could be neglected. From Figure 4 we were able to determine that the emission intensities of the cores for carbazole-based dendrimers at the same concentrations were almost equal (within experimental deviation) on excitation at 432 nm, which indicated that there was no other quenching pathway in such a system, so the photoinduced energy transfer in T(Cz-G*n*)Ps could be outlined as shown in Figure 8.

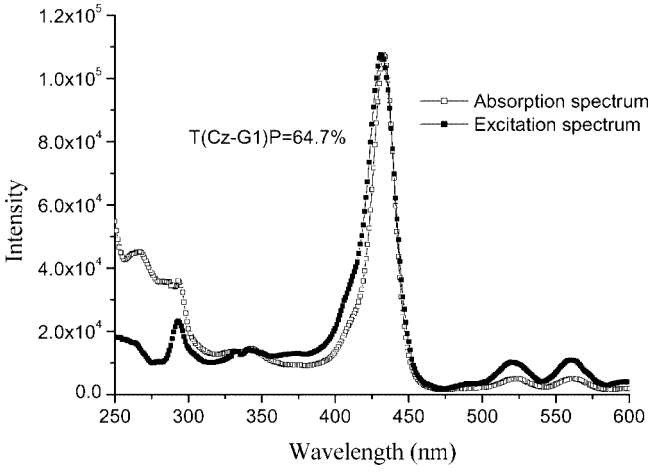



Figure 6. Absorption and corrected excitation spectra of T(Cz-G1)-P in THF monitored at the porphyrin core emission wavelength (664 nm). The excitation spectra were normalized at the Soret absorption band of the porphyrin.

The emission spectra of T(Cz-G*n*)Ps on excitation at 423 and 293 nm revealed that the dendrimers could emit intense red light. We obtained the fluorescence quantum yields ($\Phi_F$) of **1**–**3** in THF relative to TPP ($\Phi_F$ = 0.11), which were in the range from 0.199 to 0.215 and much higher than those of other porphyrins (Table 2)[3i,3l] because the carbazole units were able to reduce the self-quenching of the fluorescence of porphyrin cores.

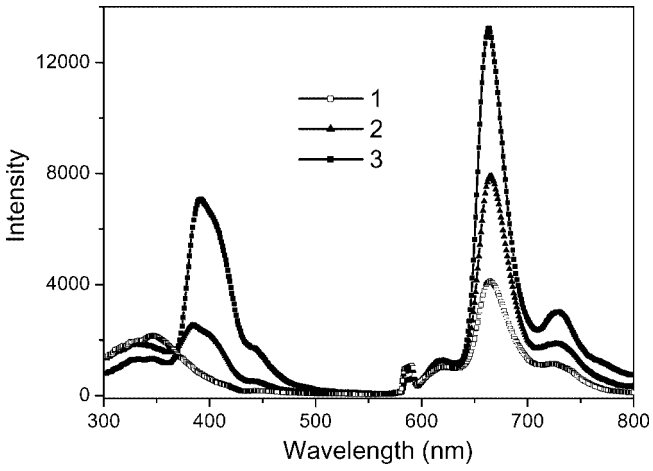



Figure 7. Emission spectra of **1**–**3** at 1 μM in THF ($\lambda_{ex}$ = 293 nm).

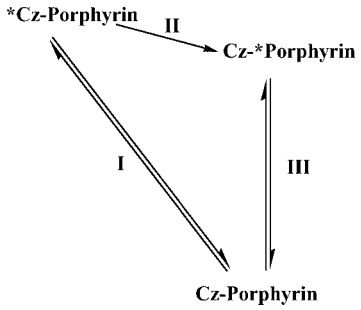



Figure 8. Schematic diagram for energy transfer in T(Cz-G*n*)Ps (**1**–**3**). (I) excited at maximum absorption of Cz (293 nm), (II) energy transfer, (III) excited at maximum absorption of porphyrin (432 nm).

Table 2.[a] Fluorescence quantum yields ($\Phi_F$) of T(Cz-G*n*)Ps **1**–**3** and TPP in THF.

| | T(Cz-G0)P (**1**) | T(Cz-G1)P (**2**) | T(Cz-G2)P (**3**) | TPP |
|---|---|---|---|---|
| $\Phi_F$ | 0.215 | 0.199 | 0.201 | 0.110 |

[a] Excitation at 423 nm.

## Conclusion

We have synthesized three dendritic carbazole-based porphyrins T(Cz-G*n*)Ps (**1**–**3**) with intramolecular energy-transfer properties. The light-harvesting abilities of these compounds increased with increasing generation number, so the T(Cz-G*n*)Ps were efficient light harvesters. The efficiency of the energy transfer, however, decreased with the generation because the energy-transfer process followed the Förster mechanism. Meanwhile, these dendritic macromolecules could emit intense red light with high fluorescence quantum yields, and so might be good candidates for photonic devices.

## Experimental Section

**General:** Tetrahydrofuran (THF) was distilled from sodium/benzophenone; other chemicals were purchased and used as received. 3-Iodocarbazole (**5**), *N*-butylcarbazole (**8**), and 3,6-bis(9′-carbazol-

yl)-9*H*-carbazole (**10**) were prepared as described in the literature.[2i,2k,4d,4e,5,6] $^1$H NMR spectra were recorded with Mercury plus 300 MHz and JEOL JNM-500EX instruments in $CDCl_3$ as solvent in all cases. UV/Vis spectra were determined with a Shimadzu UV-1601PC spectrophotometer, PL spectra were measured with a Shimadzu RF-5301 luminescence spectrometer, and IR spectra were measured with a Nicolet-360 FT-IR spectrometer by incorporation of samples in KBr disks. Mass spectra were performed with an Agilent 1100 MS series and an AXIMA CFR MALDI/TOF (matrix-assisted laser desorption ionization/time-of-flight) MS (COMPACT) instrument. The gel permeation chromatography (GPC) measurements were performed with a Waters chromatograph connected to a Waters 410 differential refractometer with THF as an eluent.

**9-Butyl-3-iodocarbazole (6):** NaH (60 wt.-%; 1.0 g, 25.0 mmol) and *n*-$C_4H_9Br$ (1.85 mL, 17.2 mmol) were added to a solution of compound **5** (5.0 g, 17.1 mmol) in DMF (30 mL). The mixture was stirred at room temperature until the reaction was complete, as monitored by TLC. The mixture was poured into water (200 mL), the precipitate collected by filtration, and recrystallized from petroleum ether to give 4.0 g (67%) of a white solid, m.p. 44.0–46.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.39 (s, 1 H, Ar–H), 8.03 (d, 1 H, Ar–H), 7.69 (d, 1 H, Ar–H), 7.50 (d, 1 H, Ar–H), 7.39 (d, 1 H, Ar–H), 7.24–7.17 (m, 2 H, Ar–H), 4.27 (t, 2 H, –$NCH_2$–), 1.78–1.88 (m, 2 H, –$CH_2$–), 1.30–1.41 (m, 2 H, –$CH_2$–), 0.94 (t, 3 H, –$CH_3$) ppm. IR (KBr):$\tilde{\nu}$ = 3048, 2956, 2924, 2856, 1619, 1588, 1473, 1458, 1345, 1331, 1273, 1213, 797, 747, 722 cm$^{-1}$. MS: calcd. 349.3; found 350.2 $[M+H]^+$.

**9-Butyl-6-iodocarbazole-3-carbaldehyde (7):** Phosphoryl chloride (4.0 g, 0.025 mol) was added slowly to DMF (5.0 g, 0.07 mol), with purging with nitrogen and cooling to 0 °C. The Vilsmeier reactant was then allowed to warm to room temperature, stirred for 1 h, and then cooled to 0 °C. After that, a solution of 9-butyl-3-iodocarbazole (**6**, 5.3 g, 0.015 mol) in 1,2-dichloroethane (13 mL) was added, and after 1 h the system was warmed to 90 °C for 8 h. Finally, the cooled solution was poured into water, extracted with $CH_2Cl_2$, and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel ($CH_2Cl_2$/hexane 3:1, v/v) to give 3.2 g (57%) of a light yellow solid; m.p. 111.0–112.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 10.09 (s, 1 H, –HC=O), 8.55 (s, 1 H, Ar–H), 8.47 (s, 1 H, Ar–H), 8.03 (d, 1 H, Ar–H), 7.78 (d, 1 H, Ar–H), 7.47 (d, 1 H, Ar–H), 7.24 (d, 1 H, Ar–H), 4.32 (t, 2 H, –$NCH_2$–), 1.88–1.83 (m, 2 H, –$CH_2$–), 1.57–1.35 (m, 2 H, –$CH_2$–), 0.96 (t, 3 H, –$CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2945, 2925, 2871, 1687, 1622, 1587, 1566, 1478, 1379 cm$^{-1}$; a strong peak at 1687 cm$^{-1}$ is the $\nu_s$ of a C=O moiety. MS: calcd. 377.2; found 378.4 $[M+H]^+$.

**9-Butylcarbazole-3-carbaldehyde (9):** The product was obtained by the procedure used for the preparation of **7** and purified by column chromatography (silica gel; hexane/ethyl acetate, 4:1, v/v). Yield 79%. M.p. 43.0–45.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 10.06 (s, 1 H, –HC=O), 8.51 (s, 1 H, Ar–H), 8.09 (d, 1 H, Ar–H), 7.96 (d, 1 H, Ar–H), 7.50 (d, 1 H, Ar–H), 7.29–7.42 (m, 3 H, Ar–H), 4.20 (t, 2 H, –$NCH_2$–), 1.76–1.83 (m, 2 H, –$CH_2$–), 1.30–1.41 (m, 2 H, –$CH_2$–), 0.94 (t, 3 H, –$CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2958, 2931, 2867, 1686, 1625, 1593, 1494, 1466, 1383 cm$^{-1}$; a strong peak at 1686 cm$^{-1}$ is the $\nu_s$ of a C=O moiety. MS: calcd. 251.3; found 252.2 $[M+H]^+$.

**9-Butyl-6-Cz1-carbazole-3-carbaldehyde (11) (Cz1 = carbazol-9-yl):** Carbazole (0.5 g, 3.0 mmol), 9-butyl-6-iodocarbazole-3-carbaldehyde (**7**, 1.0 g, 2.65 mmol), $Cu_2O$ (1.0 g, 7.0 mmol), and DMAc (7 mL) were sequentially placed in a sealed tube under nitrogen, and the mixture was heated to 190 °C in an oil bath for 24 h and then allowed to cool to room temperature and filtered. The filtrate was poured into $H_2O$ (300 mL) and stirred for 20 min, the solid was collected by filtration and recrystallized from EtOH/THF (4:1, v/v) to give a light yellow solid (0.70 g, 63%); m.p. 164.0–166.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 10.10 (s, 1 H, –HC=O), 8.59 (s, 1 H, Ar–H), 8.33 (s, 1 H, Ar–H), 8.19 (d, 2 H, Ar–H), 8.09 (d, 1 H, Ar–H), 7.67 (m, 2 H, Ar–H), 7.56 (d, 1 H, Ar–H), 7.43–7.38 (m, 4 H, Ar–H), 7.34–7.28 (m, 2 H, Ar–H), 4.56 (t, 2 H, –$NCH_2$–), 2.00–1.95 (m, 2 H, –$CH_2$–), 1.57–1.46 (m, 2 H, –$CH_2$–), 1.03 (t, 3 H, –$CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2955, 2928, 2867, 1684, 1626, 1595, 1496, 1451, 1377, 1231, 751 cm$^{-1}$; a strong peak at 1684 cm$^{-1}$ is the $\nu_s$ of a C=O moiety. MS: calcd. 416.5; found 417.1 $[M+H]^+$.

**9-Butyl-3-Cz2-carbazole (12) [Cz2 = 3,6-bis(carbazol-9-yl)carbazol-9-yl]:** Compound **12** was produced by the procedure used for the preparation of **11**, collected by filtration, and purified by column chromatography (silica gel; hexane/ethyl acetate, 10:1, v/v) to give 56 mg (68%) of a white solid; m.p. 212.0–214.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.41 (s, 1 H, Ar–H), 8.31 (s, 2 H, Ar–H), 8.16 (d, 5 H, Ar–H), 7.75–7.54 (m, 9 H, Ar–H), 7.44–7.37 (m, 8 H, Ar–H), 7.33–7.27 (m, 4 H, Ar–H), 4.46 (t, 2 H, –$NCH_2$–), 2.01–1.96 (m, 2 H, –$CH_2$–), 1.28–1.23 (m, 2 H, –$CH_2$–), 1.03 (t, 3 H, –$CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3042, 2950, 2919, 2853, 1614, 1593, 1493, 1474, 1450, 1332, 1311, 1230, 802, 748, 722 cm$^{-1}$. MS: calcd. 718.9; found 719.7 $[M+H]^+$.

**9-Butyl-6-Cz2-carbazole-3-carbaldehyde (13):** Compound **13** was produced by the procedure used for the preparation of **11**, collected by filtration, and recrystallized from EtOH/THF (4:1, v/v) to give 1.0 g (51%) of a light yellow solid; m.p. 218.0–220.0 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 10.13 (s, 1 H, –HC=O), 8.69 (s, 1 H, Ar–H), 8.49 (s, 1 H, Ar–H), 8.30 (m, 2 H, Ar–H), 8.18–8.10 (m, 5 H, Ar–H), 7.89–7.67 (m, 2 H, Ar–H), 7.64–7.50 (m, 5 H, Ar–H), 7.50–7.32 (m, 9 H, Ar–H), 7.31–7.28 (m, 3 H, Ar–H), 4.48 (t, 2 H, –$NCH_2$–), 2.02–1.96 (m, 2 H, –$CH_2$–), 1.57–1.46 (m, 2 H, –$CH_2$–), 1.05 (t, 3 H, –$CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3047, 2949, 2926, 2864, 1687, 1626, 1596, 1494, 1450, 1385, 1280, 1230, 749 cm$^{-1}$; a strong peak at 1687 cm$^{-1}$ is the $\nu_s$ of a C=O moiety. MS: calcd. 746.9; found 747.8 $[M+H]^+$.

**T(Cz-G0)P (1):** 9-Butylcarbazole-3-carbaldehyde (**9**, 1.4 g, 5.6 mmol) and *p*-nitrobenzoic acid (0.47 g, 2.8 mmol) were dissolved in xylene (45 mL). The mixture was heated to reflux, a solution of pyrrole (0.39 mL, 5.6 mmol) in xylene (5 mL) was slowly added, and the system was stirred for a further 3 h. Xylene (30 mL) was distilled from the mixture, after which MeOH (70 mL) was added. The crude product was collected by filtration and purified through a short pad of silica gel with elution with $CHCl_3$ to afford the crude porphyrin. Further chromatography (silica gel; $CHCl_3$/petroleum ether, 1:1, v/v) gave the product as a purple solid (350 mg, 21%); m.p. > 250 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.96 (s, 4 H, Ar–H), 8.89 (s, 8 H, Ar–H), 8.36 (d, 4 H, Ar–H), 8.18 (d, 4 H, Ar–H), 7.74 (d, 4 H, Ar–H), 7.60–7.52 (m, 8 H, Ar–H), 7.29–7.27 (m, 4 H, Ar–H), 4.55 (t, 8 H, –$NCH_2$–), 2.12–2.05 (m, 8 H, –$CH_2$–), 1.65–1.57 (m, 8 H, –$CH_2$–), 1.10 (t, 12 H, –$CH_3$), –2.43 (s, 2 H, –NH–) ppm. IR (KBr): $\tilde{\nu}$ = 3447, 3048, 2950, 2919, 2848, 1655, 1593, 1490, 1459, 1372, 1349, 1265, 1244, 1211, 1146, 1122, 804, 746, 727 cm$^{-1}$. MALDI-TOF: calcd. 1195.5; found 1195.4 (see Figure S1, Supporting Information).

**T(Cz-G1)P (2):** Compound **11** (0.8 g, 1.9 mmol) and *p*-nitrobenzoic acid (0.24 g, 1.4 mmol) were dissolved in xylene (30 mL). The mixture was heated to reflux, pyrrole (0.133 mL, 1.9 mmol) in xylene (5 mL) was then slowly added, and the mixture was stirred for a

further 6 h. Xylene (20 mL) was distilled from the mixture, after which MeOH (70 mL) was added. The crude product was collected by filtration and purified through a short pad of silica gel with elution with $CHCl_3$. Further chromatography (silica gel; $CHCl_3$/petroleum ether, 1:1, v/v) gave the product as a purple solid (100 mg, 11%); m.p. > 250 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.92–8.84 (m, 8 H, Ar–H), 8.44–8.29 (m, 12 H, Ar–H), 8.18–8.04 (m, 8 H, Ar–H), 7.86–7.60 (m, 12 H, Ar–H), 7.46–7.32 (m, 20 H, Ar–H), 7.21–7.19 (m, 4 H, Ar–H), 4.64 (t, 8 H, –$NCH_2$–), 2.23–2.09 (m, 8 H, –$CH_2$–), 1.74–1.59 (m, 8 H, –$CH_2$–), 1.14 (t, 12 H, –$CH_3$), –2.54 (s, 2 H, –NH–) ppm. IR (KBr): $\tilde{\nu}$ = 3442, 3052, 2945, 2919, 2848, 1650, 1593, 1492, 1477, 1451, 1342, 1286, 1230, 1148, 799, 748, 717 cm$^{-1}$. MALDI-TOF: calcd. 1856.3; found 1858.2 (see Figure S2, Supporting Information).

**T(Cz-G2)P (3):** Compound T(Cz-G2)P (**3**) was obtained as a purple solid (60 mg, 7%) by the procedure used for the preparation of T(Cz-G1)P (**2**); m.p. > 250 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 9.01–8.82 (m, 8 H, Ar–H), 8.54–8.40 (m, 12 H, Ar–H), 8.31–8.06 (m, 24 H, Ar–H), 7.99–7.93 (m, 4 H, Ar–H), 7.91–7.74 (m, 16 H, Ar–H), 7.70–7.31 (m, 56 H, Ar–H), 4.68 (t, 8 H, –$NCH_2$–), 2.22–2.11 (m, 8 H, –$CH_2$–), 1.76–1.64 (m, 8 H, –$CH_2$–), 1.16–1.09 (t, 12 H, –$CH_3$), –2.46 (s, 2 H, –NH–) ppm. IR (KBr): $\tilde{\nu}$ = 3447, 3053, 2955, 2919, 2853, 1654, 1593, 1492, 1451, 1377, 1311, 1281, 1231, 1153, 799, 748, 723 cm$^{-1}$. MALDI-TOF: calcd. 3177.8; found 3180.8 (see Figure S3, Supporting Information).

**Supporting Information** (see footnote on the first page of this article): MALDI/TOF MS and GPC spectra of compounds T(Cz-G*n*)-Ps (**1**–**3**).

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