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Synthesis and Characterization of Subporphyrins with Dendritic Carbazole Arms

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A series of novel dendritic carbazole-functionalized subporphyrins, T(Cz-G*n*)SubPs (*n* = 1–3), have been synthesized from pyridine–tri(pyrrol-1-yl)borane and the corresponding aldehydes. This study has demonstrated that intramolecular energy transfer from the carbazole dendron to the subporphyrin core occurs with a high efficiency which decreases with increasing dendron generation, in accord with the Förster mechanism of energy transfer. In addition, the carbazole dendron can lead to a blueshift of the absorption and emission bands of the subporphyrin core. The light-harvesting abilities of these compounds increase with increasing generation. Meanwhile, these dendritic macromolecules emit intense yellow-green light and may be good candidates for photonic devices.

Introduction

As an extended conjugated macrocyclic ring system, ring-expanded porphyrins have been known for many years and extensively studied on account of their unique properties and potential applications in two-photon absorption and switches.[1] It is worth noting that the first ring-contracted porphyrin, subporphyrin, was prepared by Osuka and co-workers under harsh reaction conditions as recently as 2006.[2] Subsequently, more versatile and facile synthetic methods for the synthesis of *meso*-aryl-subporphyrins have been developed by Kobayashi and Osuka and their coworkers, but it is still a great challenge to introduce desired functional groups such as dendritic substituents into subporphyrins.[3] The subporphyrin features a 14π-electron aromatic core, but nonetheless adopts a nonplanar cone-shaped conformation. It is also the porphyrinic counterpart of subphthalocyanines whose optoelectronic properties can be fine-tuned by varying their axial X ligands or by functionalizing peripheral substituents.[2–4] Thus, it is possible that the introduction of functional moieties as arms into the subporphyrin core will provide some fantastic properties.

The synthesis of dendrimers, cascade molecules, and related hyper-branched systems, as well as their characterization, is currently attracting great interest in the field of materials science.[5] Dendrimers are monodisperse, highly branched macromolecules with well-defined three-dimensional structures which are constructed from an interior core with a regular array of branching units. There has been considerable interest in the incorporation of functional units onto the exterior surface or into the interior of dendrimers. It is well known that a dendritic framework can affect several functionalities by controlling the microenvironments around the functional units.[6,7] In addition, carbazole is an attractive molecule because of its intense luminescence, electron sufficiency, and potential for dendritic construction.[8–10] Therefore, novel dendrimers based on carbazole as the repeating unit and the subporphyrin as the core may exhibit fascinating photophysical and electronic properties. To the best of our knowledge, there is no example of a subporphyrin *meso*-linked to a rigid dendron. Herein, we present the synthesis of a series of well-defined subporphyrins with three dendritic carbazole arms (Scheme 1) and an investigation of their photophysical properties.

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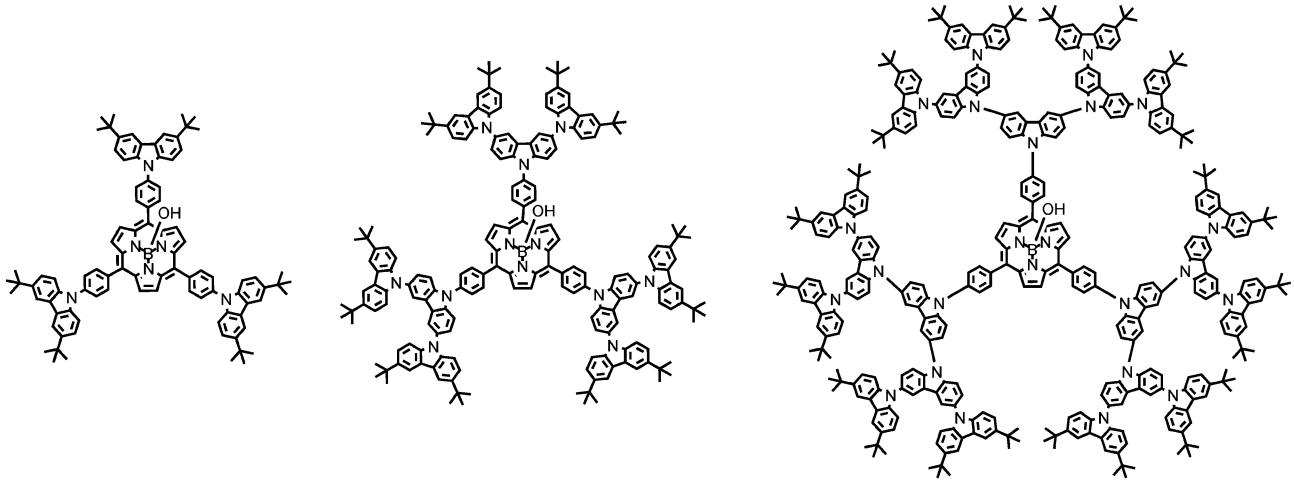
Results and Discussion

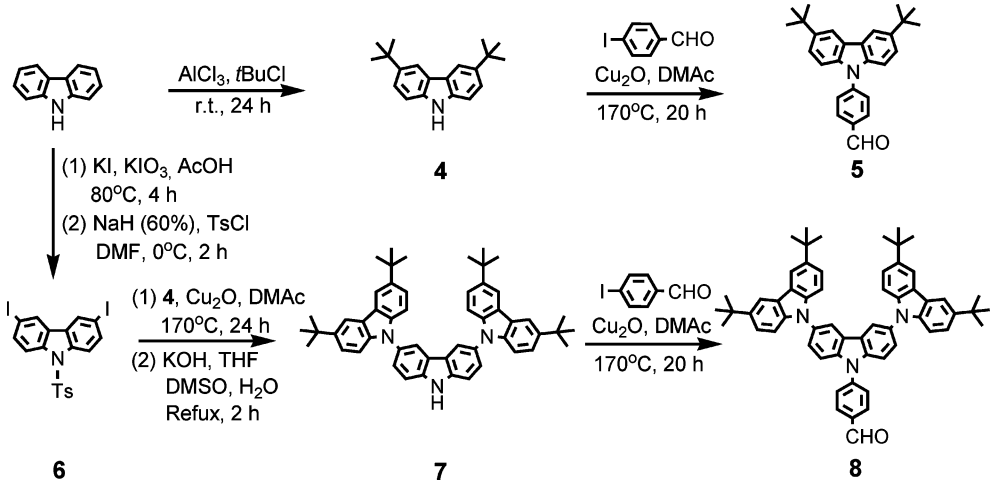
Synthesis of the Carbazole-Based Dendrons

The synthetic routes to the precursors of aldehydes **5**, **8**, and **11** are shown in Scheme 2, Scheme 3, and Scheme 4. To improve the solubility and stability of the molecules, *tert*-butyl groups were introduced into the 3,6-positions of the peripheral carbazoles in the dendrons. 3,6-Di-*tert*-butylcarbazole (**4**) was prepared in a yield of 54% by Friedel–Crafts alkylation of carbazole by adaptation of a published procedure.[11] The first-generation carbazole dendron **5** (Cz–G1–CHO) was obtained from compound **4** and *p*-iodobenzaldehyde, catalyzed by Cu_2O in *N*,*N*-dimethylacetamide (DMAc) at 170 °C for 20 h, by the Ullmann conden-



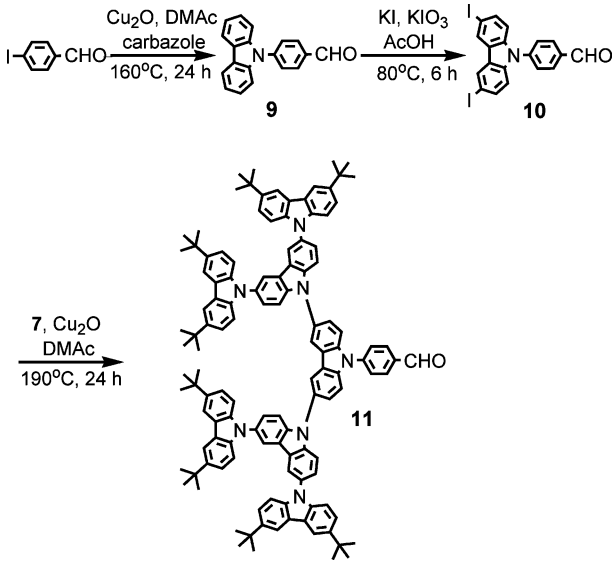
T(Cz-G1)SubP 1 T(Cz-G2)SubP 2 T(Cz-G3)SubP 3

Scheme 1. Molecular structures of T(Cz-G*n*)SubPs **1**–**3**.



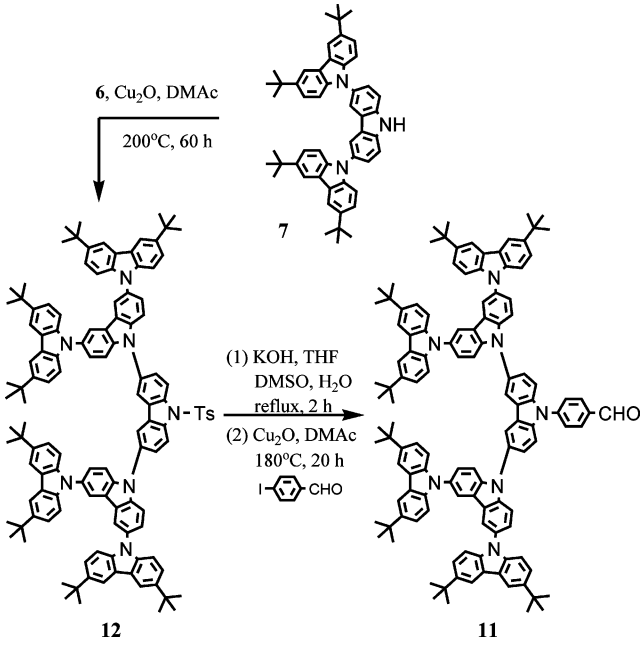
Scheme 2. Synthesis of Cz–G1–CHO (**5**) and Cz–G2–CHO (**8**).

sation reaction in a yield of 75%.[7k,8b,8c,10] The second-generation carbazole dendron **8** (Cz–G2–CHO) was synthesized from compound **7** and *p*-iodobenzaldehyde under similar conditions in a yield of 72%, while compound **7** was synthesized from compounds **4** and **6** through an Ullmann coupling reaction followed by cleavage of the N–Ts bond under basic conditions (70%, two steps).[7k,8b,8c,10] The first synthetic route we chose for the preparation of the third-generation carbazole dendron **11** (Cz–G3–CHO) is shown in Scheme 3. The iodination of compound **9**, which was obtained from the Ullmann condensation reaction of carbazole and *p*-iodobenzaldehyde, was pursued to give compound **10**.[10c] Compound **11** was obtained in a low yield (10%) through the Ullmann condensation reaction of compounds **10** and **7** at 190 °C for 24 h. To explain the low yield it was proposed that the aldehyde groups were partially oxidized by Cu_2O under the experimental conditions and would have been completely oxidized above 190 °C for 24 h. If the temperature was lowered or the reaction time shortened the amount of mono adduct, whose solubility and po-



Scheme 3. Synthesis of Cz–G3–CHO (**11**).

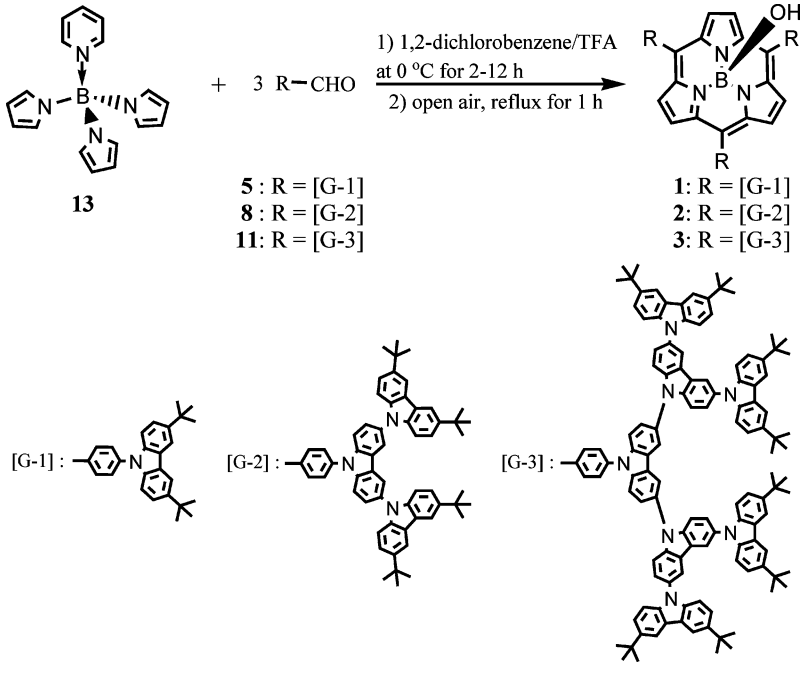
larity are similar to those of the double adduct, would be increased. Therefore, another synthetic route was designed and amended to improve the yield and simplify the purification of **11** (Scheme 4). The Ullmann condensation reaction between compound **6** and **7** was carried out at 200 °C for 60 h to obtain compound **12**, which was recrystallized from EtOH/THF (1:1, v/v) twice to give a yield of 65%. Compound **12** was previously synthesized in a yield of only 14% due to the lower reactivity and easier oxidation of the larger carbazole oligomers.[8b] It was found that the use of a sealed tube could avoid oxidation at a higher temperature.[10] Compound **12** was treated with KOH in mixed solvents to remove the Ts group and the resulting product was condensed with *p*-iodobenzaldehyde at 180 °C for 20 h to give the third-generation carbazole dendron **11** which was recrystallized from EtOH/THF (4:1, v/v) in a yield of 70% after chromatography using petroleum ether/CH_2Cl_2 (1:2, v/v) as the eluent.



Scheme 4. Improved synthetic route to Cz–G3–CHO (**11**).

Synthesis of the Dendrimers

The synthetic routes to the dendritic subporphyrins **1**–**3** are outlined in Scheme 5. First, we tried the Adler reaction conditions which are effective for the preparation of *meso*-aryl-subporphyrins[3a–3c] but failed in this application. The reason for this might be that more time is required for the reaction between pyridine–tri(pyrrol-1-yl)borane (**13**) and the large-volume aldehyde (in this case the dendritic aldehyde),[12] but also a major side-reaction involving the acid-promoted scrambling of **13** under such harsh condition takes place, suppressing the formation of the dendritic subporphyrins. Osuka and co-workers presented another method for the synthesis of subporphyrins which involved a one-pot two-step reaction under milder conditions.[3b] Accordingly, **13** and 3 equivs. of Cz–G1–CHO (**5**) were condensed in the presence of trifluoroacetic acid (TFA) at 0 °C under N_2 for 2 h in order to avoid the acid-promoted scrambling. During the reaction process the color of the mixture changed from light-yellow to deep-red.[13] After being quenched with pyridine, the reaction mixture was refluxed in *o*-dichlorobenzene for 1 h to complete the air-oxidation. Dendrimer **1** was obtained in only 2% yield after a tedious purification procedure based on multiple column



Scheme 5. Synthesis of T(Cz-G*n*)SubPs **1**–**3**.

chromatography steps. Dendrimers **2** and **3** were similarly synthesized from Cz–G2–CHO (**8**) and Cz–G3–CHO (**11**) in yields of 2.2 and 1.4%, respectively. With increasing generation of the dendron, the volume of the aldehydes became larger, and the reaction time was lengthened to 6 and 12 h for the condensation reactions of **13** with Cz–G2–CHO (**8**) and Cz–G3–CHO (**11**), respectively. Since the dendritic subporphyrins in B–OH forms were strongly adsorbed by silica gel, the pure products were obtained by column chromatography once on silica gel and twice on alumina. All the dendritic subporphyrins are readily soluble in many common organic solvents including petroleum ether, CH_2Cl_2, chloroform, THF, and toluene. All the new compounds were characterized unambiguously by FT-IR, ^1H and ^{13}C NMR, C,H,N elemental analyses, and MALDI-TOF mass spectrometry (see the electronic supporting information).

Optical Properties of the T(Cz-G*n*)SubPs

Figure 1 shows the UV/Vis absorption spectra of compounds **1**–**3**. Several absorption bands in the visible region are observed, including two Q-bands in the range of 450–530 nm together with a Soret band at around 380 nm and others in the UV region (250–350 nm) due to the carbazole units. The absorbance of the carbazole units is clearly proportional to their increased number in each generation which indirectly reflects the structural flawlessness of the as-synthesized dendrimers. Compared with the *meso*-phenylsubporphyrin, the Soret bands of the dendritic subporphyrins **1**–**3** are redshifted from 373 to 390, 381, and 380 nm, respectively.[3a] Significantly, the Soret bands of **1**–**3** are blueshifted with increasing generation of the dendron (Table 1). This may be due to the larger volume of carbazole dendron in compounds **2** and **3** which can enlarge the dihedral angle and weaken the degree of conjugation between the subporphyrin ring and the carbazole dendrons.[3b] Similarly, the emission bands of the dendrimers in dilute solution are also blueshifted with increasing generation under excitation of the subporphyrin core, for example, the emission bands of **1**–**3** appear at 556, 545, and 537 nm, respectively (Figure 2 and Table 1).[3a] The emission of the carbazole units at around 420 nm was significantly weakened when **1**–**3** were selectively excited at 299 nm, whereas a strong emission ascribed to the subporphyrin cores was observed (Figure 3) which indicates effective intramolecular energy transfer from the carbazole units to the subporphyrin core. The efficiency of the energy transfer (Φ_{ET}) can be estimated by comparing the absorption and excitation spectra of the dendron units.[14] The Φ_{ET} values of **1**–**3** are 82, 77, and 60%, respectively (see Figures S1–S3 and Table 1). Clearly, the energy-transfer efficiency decreases with increasing generation of the dendrimers. This trend can be ascribed, in the context of the Förster mechanism of energy transfer, to the influence of the distance between the donor and the acceptor, the overlap integral between the carbazole-based dendrons and the subporphyrin core.[6a] With an increase in energy-transfer distance, the efficiency would very likely drop by several orders of magnitude if the transfer takes place in a single hop, so energy transfer in the large dendritic subporphyrins may occur in several steps. Hence, the larger transfer distance in this dendritic system is significant because it introduces more energy-transfer steps. Furthermore, the emission intensity of the subporphyrin core increases from **1** to **3** under excitation at 299 nm. This can be explained by the fact that the growing number of carbazoles in the higher generation dendrimers results in increasing absorption. All the dendritic subporphyrins **1**–**3** exhibit strong fluorescence emission. The fluorescence quantum yields were determined by using quinine sulfate as a standard and the Φ_F values for **1**–**3** in $CHCl_3$ are 0.154, 0.136, and 0.110 (Table 1), respectively, similar to that of the *meso*-phenylsubporphyrin.[3a]

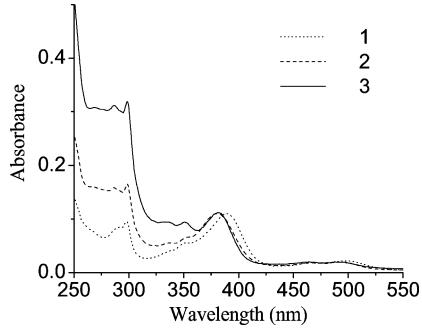


Figure 1. UV/Vis absorption spectra (normalized at the Soret bands) of **1**–**3** in $CHCl_3$.

Table 1. Photophysical data for T(Cz-G*n*)SubPs **1**–**3** in $CHCl_3$.

Dendrimers	λ_{abs}^{max} [nm]	$\lambda_{em}^{max[a]}$ [nm]	Φ_{ET}[b] [%]	Φ_F[c]
T(Cz-G1)SubP (**1**)	298, 353, 390, 471, 498	556	82	0.154
T(Cz-G2)SubP (**2**)	299, 353, 381, 468, 494	545	77	0.136
T(Cz-G3)SubP (**3**)	299, 351, 380, 465, 492	537	60	0.110

[a] Excited at 299 nm. [b] Energy-transfer efficiency (Φ_{ET}) was calculated by comparing the absorption and excitation spectra of the dendrimers by monitoring the emission of the subporphyrin core. [c] The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 0.546, λ = 366 nm) as the standard.

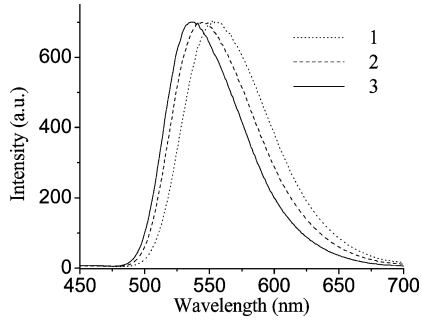


Figure 2. Normalized emission spectra of **1**–**3** in $CHCl_3$ (λ_{ex} = 390 nm for **1**, λ_{ex} = 381 nm for **2** and **3**).

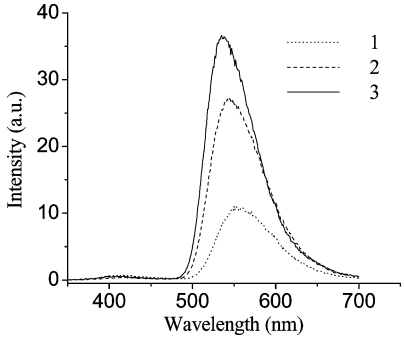


Figure 3. Emission spectra of 1 μM **1**–**3** in $CHCl_3$ (λ_{ex} = 299 nm).

Conclusion

Versatile synthetic routes to subporphyrins with dendritic carbazole arms T(Cz-G*n*)SubPs **1**–**3** by one-pot two-step reactions from pyridine–tri(pyrrol-1-yl)borane and the corresponding aldehydes have been explored. A rigorous and tedious purification procedure based on multiple chromatography steps is required to obtain **1**–**3**. The intramolecular energy transfer from the carbazole dendron to the subporphyrin core occurs with a high efficiency, which decreases with increasing generation of the dendron, in accord with the Förster mechanism of energy transfer. In addition, the light-harvesting abilities of these compounds increase with increasing generation. The energy transfer in the large dendritic subporphyrins occurs in several transfer steps. The carbazole dendron can significantly influence the absorption and emission bands of the subporphyrin core, which are blueshifted with increasing generation of the dendron. Meanwhile, these dendritic macromolecules emit intense yellow-green light and may be good candidates for photonic devices.

Experimental Section

Ether and benzene were freshly distilled from sodium and benzophenone. Pyrrole was distilled from sodium and pyridine was distilled from CaH_2. *N*,*N*-Dimethylacetamide (DMAc) was dried with P_2O_5. Other chemicals were used as received. 3,6-Di-*tert*-butyl-9*H*-carbazole (**4**),[11] 3,6-diiodo-9-tosyl-9*H*-carbazole (**6**),[10c] and compound **7**[71,8c] were prepared according to the literature. Tri(pyrrol-1-yl)borane was prepared from $LiBH_4$ and pyrrole by the reported procedure and was converted into pyridine–tri(pyrrol-1-yl)borane (**13**) by treatment with dry pyridine under N_2.[12] ^1H and ^{13}C NMR spectra were recorded with a Mercury plus spectrometer at 500 and 125 MHz, respectively, using $CDCl_3$ as solvent in all cases. UV/Vis spectra were determined with a Shimadzu UV-1601PC spectrophotometer. Photoluminescence (PL) spectra were recorded with a Shimadzu RF-5301 Luminescence spectrometer. IR spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr disks. Mass spectra were performed with an Agilent 1100 and AXIMA CFR MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) mass spectrometers (COMPACT). C,H,N elemental analyses were measured with a Perkin-Elmer 240C elemental analyzer.

4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)benzaldehyde (5): 3,6-Di-*tert*-butyl-9*H*-carbazole (**4**) (2.79 g, 10 mmol), 4-iodobenzaldehyde (2.6 g, 11.2 mmol), Cu_2O (2.8 g, 19.4 mmol), and DMAc (8 mL) were added sequentially to a sealed tube under nitrogen and heated at 170 °C in an oil bath for 20 h. Then the mixture was cooled 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 petroleum ether to give 3.1 g (75%) of a light-yellow solid, m.p. 159.0–160.0 °C. IR (KBr): $\tilde{\nu}$ = 3049.1, 2962.3, 2902.5, 2865.8, 2732.8, 1699.1, 1600.7, 1512.0, 1471.5, 1369.3, 1324.9, 1296.0, 1263.2, 1234.3, 1205.4, 1161.0, 1103.1, 1035.6, 885.2, 810.0, 727.1 cm^{-1}. The strong peak at 1699.1 cm^{-1} is the vs of the C=O moiety. ^1H NMR ($CDCl_3$, 500 MHz): δ = 10.11 (s, 1 H, -CHO), 8.32 (s, 2 H, Ar-H), 8.19 (d, J = 8.5 Hz, 2 H, Ar-H), 7.90 (d, J = 8.5 Hz, 2 H, Ar-H), 7.52 (d, J = 9.0 Hz, 2 H, Ar-H), 7.46 (d, J = 9.0 Hz, 2 H, Ar-H), 1.42 (s, 18 H, $-CH_3$) ppm (see Figures S9 and S10). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 191.0, 143.9, 138.4, 134.1, 131.3, 126.2, 124.1, 116.5, 109.3, 34.8, 31.9 ppm (see Figure S25). MS: calcd. 383.5; found 384.3 [M^+ + H]. $C_{27}H_{29}NO$ (383.53): calcd. C 84.55, H 7.62, N 3.65; found C 84.50, H 7.75, N 3.61.

4-[3,6-Bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]benzaldehyde (8): 3,6-Di-*tert*-butyl-9-[3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-6-yl]-9*H*-carbazole (**7**) (4.1 g, 5.7 mmol), 4-iodobenzaldehyde (1.8 g, 7.8 mmol), Cu_2O (1.8 g, 12.5 mmol), and DMAc (10 mL) were added sequentially to a sealed tube under nitrogen and heated at 170 °C in an oil bath for 20 h. Then the mixture was cooled to room temperature and filtered. The filtrate was poured into H_2O (400 mL) and stirred for 20 min. The solid was collected by filtration and purified by chromatography (silica gel, petroleum ether/ethyl acetate, 20:1, v/v) to give 4.0 g of a light-yellow solid which was further recrystallized from EtOH/THF (4:1, v/v) to give 3.4 g (72%) of a light-yellow solid, m.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3051.0, 2962.3, 2902.5, 2865.8, 2738.6, 1701.0, 1600.7, 1490.8, 1365.4, 1324.9, 1297.9, 1263.2, 1236.2, 1203.4, 1161.0, 1105.1, 879.4, 810.0 cm^{-1}. The strong peak at 1701.0 cm^{-1} is the vs of the C=O moiety. ^1H NMR ($CDCl_3$, 500 MHz): δ = 10.19 (s, 1 H, -CHO), 8.24 (d, J = 8.0 Hz, 4 H, Ar-H), 8.16 (s, 4 H, Ar-H), 7.97 (d, J = 8.0 Hz, 2 H, Ar-H), 7.72 (d, J = 8.5 Hz, 2 H, Ar-H), 7.64 (d, J = 10.5 Hz, 2 H, Ar-H), 7.45 (d, J = 8.5 Hz, 4 H, Ar-H), 7.33 (d, J = 10.5 Hz, 4 H, Ar-H), 1.40 (s, 36 H, $-CH_3$) ppm (see Figures S13 and S14). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 190.8, 142.8, 142.7, 140.0, 139.6, 135.2, 131.7, 131.6, 127.0, 126.2, 124.6, 123.6, 123.2, 119.4, 116.3, 111.1, 109.0, 34.7, 32.0 ppm (see Figure S26). MS (MALDI-TOF): calcd. 826.1; found 825.6 (see Figure S4). $C_{59}H_{59}N_3O$ (826.12): calcd. C 85.78, H 7.20, N 5.09; found C 85.80, H 7.31, N 5.20.

4-(9*H*-Carbazol-9-yl)benzaldehyde (9): Carbazole (3.34 g, 20 mmol), 4-iodobenzaldehyde (5.0 g, 21.6 mmol), Cu_2O (4.0 g, 27.8 mmol), and DMAc (15 mL) were added sequentially to a sealed tube under nitrogen and heated at 160 °C in an oil bath for 20 h. Then the mixture was cooled 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 to give 4.1 g (76%) of a light-yellow solid, m.p. 156.0–158.0 °C. IR (KBr): $\tilde{\nu}$ = 3049.1, 2821.5, 2732.8, 1702.9, 1596.8, 1512.0, 1450.3, 1361.6, 1336.5, 1317.2, 1226.6, 1209.2, 1161.0, 1103.1, 829.3, 750.2 cm^{-1}. The strong peak at 1702.9 cm^{-1} is the vs of the C=O moiety. ^1H NMR ($CDCl_3$, 500 MHz): δ = 10.14 (s, 1 H, -CHO), 8.29 (d, J = 8.0 Hz, 2 H, Ar-H), 8.22 (d, J = 8.0 Hz, 2 H, Ar-H), 7.92 (d, J = 8.5 Hz, 2 H, Ar-H), 7.54 (d, J = 8.5 Hz, 2 H, Ar-H), 7.49 (t, J = 14.5 Hz, 2 H, Ar-H), 7.36 (t, J = 14.5 Hz, 2 H, Ar-H) ppm (see Figure S11). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 191.0, 143.3, 140.0, 134.6, 131.3, 126.7, 126.2, 124.0, 120.8, 120.5, 109.7 ppm (see Figure S27). MS: calcd. 271.3; found 272.5 [M +

H]$^+$. $C_{19}H_{13}NO$ (271.31): calcd. C 84.11, H 4.83, N 5.16; found C 84.14, H 4.75, N 5.20.

4-(3,6-Diiodo-9*H*-carbazol-9-yl)benzaldehyde (10): Compound **9** (3.0 g, 11.1 mmol) was dissolved in refluxing acetic acid (75 mL). The solution was cooled to 80 °C, KI (2.48 g, 14.9 mmol) and KIO_3 (1.8 g, 8.4 mmol) were added, and the system was maintained at 80 °C for another 5 h. After that, the mixture was cooled to room temperature, filtered, and then the collected solid was poured into 5% $NaHSO_3$ (200 mL) to remove I_2 and KIO_3. The solid was collected by filtration and recrystallized from THF to give 4.8 g (82%) of a light-yellow solid, m.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3056.8, 2833.1, 2740.5, 1699.1, 1596.8, 1508.1, 1465.7, 1425.2, 1359.6, 1313.4, 1274.8, 1224.6, 1207.3, 1161.0, 1018.3, 865.9, 829.3, 796.5 cm^{-1}. The strong peak at 1699.1 cm^{-1} is the νs of the C=O moiety. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 10.14 (s, 1 H, -CHO), 8.76 (s, 2 H, Ar-H), 8.21 (d, J = 8.0 Hz, 2 H, Ar-H), 7.90 (d, J = 8.0 Hz, 2 H, Ar-H), 7.77 (d, J = 8.5 Hz, 2 H, Ar-H), 7.35 (d, J = 8.5 Hz, 2 H, Ar-H) ppm (see Figure S12). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 190.7, 142.2, 139.4, 135.3, 134.5, 131.5, 129.6, 126.9, 125.0, 111.8, 83.8 ppm (see Figure S28). MS: calcd. 523.1; found 523.8 [M + H]$^+$. $C_{19}H_{11}I_2NO$ (523.11): calcd. C 43.62, H 2.12, N 2.68; found C 43.40, H 2.26, N 2.72.

4-{3,6-Bis[3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}benzaldehyde (11): 3,6-Di-*tert*-butyl-9-[3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-6-yl]-9*H*-carbazole (**7**) (5.0 g, 6.9 mmol), 4-(3,6-diiodo-9*H*-carbazol-9-yl)benzaldehyde (**10**) (1.5 g, 2.9 mmol), Cu_2O (2.1 g, 14.6 mmol), and DMAc (20 mL) were added sequentially to a sealed tube under nitrogen and heated at 190 °C in oil bath for 24 h. Then the mixture was cooled to room temperature and filtered. The filtrate was poured into H_2O (400 mL) and stirred for 20 min. The solid was collected by filtration and was purified by chromatography (silica gel, petroleum ether/CH_2Cl_2, 1:2, v/v) to give 1.9 g of a white solid which was further recrystallized three times from EtOH/THF (2:1, v/v) to give 0.5 g (10%) of a white solid, m.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3047.1, 2960.3, 2902.5, 2865.8, 1704.8, 1600.7, 1490.8, 1363.5, 1323.0, 1296.0, 1263.2, 1232.4, 1162.9, 1033.7, 877.5, 810.0 cm^{-1}. The strong peak at 1704.8 cm^{-1} is the νs of the C=O moiety. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 10.23 (s, 1 H, -CHO), 8.56 (s, 2 H, Ar-H), 8.32–8.27 (m, 6 H, Ar-H), 8.15 (s, 8 H, Ar-H), 8.04 (d, J = 8.0 Hz, 2 H, Ar-H), 7.87 (s, 4 H, Ar-H), 7.65–7.60 (m, 8 H, Ar-H), 7.44 (d, J = 8.5 Hz, 8 H, Ar-H), 7.33 (d, J = 8.5 Hz, 8 H, Ar-H), 1.45 (s, 72 H, -CH_3) ppm (see Figures S15 and S16). ^{13}C NMR ($CDCl_3$, 125 MHz): (see Figure S29). MS (MALDI-TOF): calcd. 1711.3; found 1712.3 (see Figure S5). $C_{123}H_{119}N_7O$ (1711.31): calcd. C 86.33, H 7.01, N 5.73; found C 86.17, H 6.92, N 5.81.

3,6-Bis[3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9-tosyl–9*H*-carbazole (12): 3,6-Di-*tert*-butyl-9-[3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9*H*-carbazol-6-yl]-9*H*-carbazole (**7**) (5.0 g, 6.9 mmol), 3,6-diiodo-9-tosyl-9*H*-carbazole (**6**) (1.7 g, 2.9 mmol), Cu_2O (2.1 g, 14.6 mmol), and DMAc (20 mL) were added sequentially to a sealed tube under nitrogen and heated at 200 °C in an oil bath for 60 h. Then the mixture was cooled to room temperature and filtered. The filtrate was poured into H_2O (400 mL) and stirred for 20 min. The solid was collected by filtration and recrystallized twice from EtOH/THF (4:1, v/v) to give 3.4 g (65%) of a white solid, m.p. >250 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.75 (d, J = 8.5 Hz, 2 H, Ar-H), 8.36 (s, 2 H, Ar-H), 8.25 (s, 4 H, Ar-H), 8.15 (s, 8 H, Ar-H), 8.03 (d, J = 8.0 Hz, 2 H, Ar-H), 7.95 (d, J = 8.5 Hz, 2 H, Ar-H), 7.60 (s, 8 H, Ar-H), 7.44 (d, J = 8.0 Hz, 8 H, Ar-H), 7.38–7.32 (m, 10 H, Ar-H), 2.43 (s, 3 H, -CH_3), 1.45 (s, 72 H, -CH_3) ppm (see Figures S17 and S18). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 142.6, 140.8, 140.1, 138.2, 133.6, 131.1, 130.2, 127.4, 127.1, 126.8, 126.1, 124.0, 123.6, 123.1, 119.5, 116.7, 116.2, 110.9, 109.0, 34.7, 32.0 ppm (see Figure S30). $C_{123}H_{121}N_7O_2S$ (1761.39): calcd. C 83.87, H 6.92, N 5.57; found C 83.68, H 6.97, N 5.55.

Improved Procedure for the Synthesis of Compound 11: Compound **12** (3.0 g, 1.7 mmol) was dissolved in THF (20 mL), DMSO (10 mL), and H_2O (2 mL), and then KOH (2.0 g, 35.7 mmol) was added. The mixture was refluxed for 4 h (monitored by TLC), cooled to room temperature, neutralized by HCl, and then poured into water to give the tosyl-deprotected product of **12** as a white solid in a quantitative yield. Then the obtained products (2.7 g, 1.7 mmol), 4-iodobenzaldehyde (1.0 g, 4.3 mmol), Cu_2O (1.3 g, 9.0 mmol), and DMAc (10 mL) were added sequentially to a sealed tube under nitrogen and heated at 180 °C in oil bath for 20 h. Then the mixture was cooled to room temperature and filtered. The filtrate was poured into H_2O (400 mL) and stirred for 20 min. The solid was collected by filtration, purified by chromatography (silica gel, petroleum ether/CH_2Cl_2, 1:2, v/v), and recrystallized from EtOH/THF (4:1, v/v) to give 2.0 g (70%) of a light-yellow solid. The characterization data was the same as those listed above.

***meso*-Tris(Cz-G1)subporphyrin (1):** Cz–G1–CHO (**5**) (1.2 g, 3.13 mmol) was added to a suspension of pyridine–tri(pyrrol-1-yl)-borane (**13**) (300 mg, 1.04 mmol) in 1,2-dichlorobenzene (45 mL) and the mixture was cooled to 0 °C in an ice bath. After the dropwise addition of trifluoroacetic acid (0.085 mL, 1.10 mmol) through a syringe, the mixture immediately turned from light-yellow to deep-red and was stirred for 2 h at 0 °C under N_2. Then the acid was quenched with pyridine (0.1 mL) and the resulting solution was heated at reflux for 1 h. The solvent was removed by distilling the mixture. The resulting black tar was purified by chromatography (silica gel, CH_2Cl_2 as an eluent) to afford crude **1**. Further chromatography (alumina, from CH_2Cl_2 to CH_2Cl_2/ethyl acetate, 1:20, v/v as eluent) twice gave **1** as a brown-orange solid (28 mg, 2.0%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.34–8.32 (d, 12 H, Ar-H), 8.22 (s, 6 H, β-H), 7.96 (d, J = 7.0 Hz, 6 H, Ar-H), 7.67 (d, J = 8.5 Hz, 6 H, Ar-H), 7.57 (d, J = 8.5 Hz, 6 H, Ar-H), 1.52 (s, 54 H, -CH_3), –2.53 (s, 1 H, -OH) ppm (see Figures S19 and S20). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 143.2, 140.4, 139.1, 138.2, 135.6, 134.3, 130.5, 126.7, 123.8, 122.6, 119.8, 116.4, 109.4, 34.8, 32.0 ppm (see Figure S31). MS (MALDI-TOF): calcd. 1302.6 [M – OH]$^+$; found 1302.5 [M – OH]$^+$ (see Figure S6). $C_{93}H_{91}BN_6O$ (1319.57): calcd. C 84.65, H 6.95, N 6.37; found C 84.36, H 7.03, N 6.44.

***meso*-Tris(Cz-G2)subporphyrin (2):** Cz–G2–CHO (**8**) (1.7 g, 2.06 mmol) was added to a suspension of pyridine–tri(pyrrol-1-yl)-borane (**13**) (200 mg, 0.70 mmol) in 1,2-dichlorobenzene (30 mL) and the mixture was cooled to 0 °C in an ice bath. After the dropwise addition of trifluoroacetic acid (0.056 mL, 0.73 mmol) through a syringe, the solution was stirred for 6 h at 0 °C in the dark under N_2. The mixture slowly turned from light-yellow to deep-red. The acid was quenched with pyridine (0.07 mL) and the resulting solution was heated at reflux. After 1 h the solvent was removed by distillation from the mixture. The resulting black tar was purified by chromatography (silica gel, CH_2Cl_2 as an eluent) to afford crude **2**. Further chromatography (alumina, from CH_2Cl_2/petroleum ether, 1:1, to CH_2Cl_2/petroleum ether, 3:1, v/v as eluent) twice gave **2** as a brown-orange solid (40 mg, 2.2%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.50 (m, 6 H, Ar-H), 8.44 (s, 6 H, Ar-H), 8.33 (s, 6 H, Ar-H), 8.18 (s, 18 H, Ar-H and β-H), 7.97 (d, J = 8.5 Hz, 6 H, Ar-H), 7.74 (d, J = 8.5 Hz, 6 H, Ar-H), 7.48 (d, J = 8.5 Hz, 12 H, Ar-H), 7.40 (d, J = 8.5 Hz, 12 H, Ar-H), 1.48 (s, 108 H, -CH_3) ppm (see Figures S21 and S22). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 142.6, 140.5, 140.3, 140.1, 137.4, 136.8, 134.7, 131.3,

127.3, 126.2, 124.3, 123.6, 123.1, 122.8, 119.6, 119.5, 116.3, 111.4, 109.1, 34.8, 32.1 ppm (see Figure S32). MS (MALDI-TOF): calcd. 2630.5 $[M - OH]^+$; found 2629.4 $[M - OH]^+$ (see Figure S7). $C_{189}H_{181}BN_{12}O$ (2647.35): calcd. C 85.75, H 6.89, N 6.35; found C 85.98, H 6.80, N 6.39.

***meso*-Tris(Cz-G3)subporphyrin (3):** Cz–G3–CHO (**11**) (1.8 g, 1.05 mmol) was added to a suspension of pyridine–tri(pyrrol-1-yl)-borane (**13**) (100 mg, 0.35 mmol) in 1,2-dichlorobenzene (35 mL) and the mixture was cooled to 0 °C in an ice bath. After the dropwise addition of trifluoroacetic acid (0.03 mL, 0.39 mmol) through a syringe, the solution was stirred at 0 °C for 12 h and stirred at room temperature for 2 h in the dark under N_2. The mixture turned from light-yellow to deep-red very slowly. The acid was quenched with pyridine (0.05 mL) and the resulting solution was heated at reflux. After 1 h the solvent was removed by distillation from the mixture. The resulting black tar was purified by chromatography (silica gel, toluene as eluent) to afford crude **3**. Further chromatography (alumina, from toluene to CH_2Cl_2/petroleum ether, 1:1, v/v as eluent) twice gave **3** as a brown-orange solid (26 mg, 1.4%). ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.64 (s, 6 H, Ar-H), 8.59 (s, 6 H, Ar-H), 8.52 (s, 6 H, Ar-H), 8.30 (s, 12 H, Ar-H), 8.16 (s, 24 H, Ar-H), 7.97 (d, J = 8.0 Hz, 6 H, Ar-H), 7.71 (d, J = 8.0 Hz, 18 H, Ar-H), 7.64 (d, J = 8.0 Hz, 12 H, Ar-H), 7.53 (s, 6 H, β-H), 7.45 (d, J = 8.5 Hz, 24 H, Ar-H), 7.36 (d, J = 8.5 Hz, 24 H, Ar-H), 1.47 (s, 216 H, -CH_3) ppm (see Figures S23 and S24). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 142.6, 141.3, 141.1, 140.6, 140.2, 135.0, 132.5, 132.3, 130.9, 130.4, 128.8, 126.6, 126.1, 124.5, 123.8, 123.5, 123.1, 120.2, 119.5, 116.2, 111.9, 111.0, 109.1, 34.7, 32.0 ppm (see Figure S33). MS (MALDI-TOF): calcd. 5281.9 $[M - OH]^+$; found 5279.1 $[M - OH]^+$ (see Figure S8). $C_{381}H_{361}BN_{24}O$ (5302.91): calcd. C 86.29, H 6.86, N 6.34; found C 86.02, H 7.22, N 6.17.

Supporting Information (see also the footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all new compounds and MALDI-TOF MS spectra of compounds **1**–**3**, **8**, and **11**.

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[1] a) J. L. Sessler, D. Seidel, *Angew. Chem. Int. Ed.* **2003**, *42*, 5134–5175; b) T. K. Chadrashekar, S. Venkatraman, *Acc. Chem. Res.* **2003**, *36*, 676–691; c) M. Suzuki, A. Osuka, *Org. Lett.* **2003**, *5*, 3943–3946; d) S. Shimizu, N. Aratani, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 4909–4918; e) M. Suzuki, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 464–465.

[2] Y. Inokuma, J. H. Kwon, T. K. Ahn, M. C. Yoo, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2006**, *45*, 961–964.

[3] a) N. Kobayashi, Y. Takeuchi, A. Matsuda, *Angew. Chem. Int. Ed.* **2007**, *46*, 758–760; b) Y. Inokuma, Z. S. Yoon, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 4747–4761; c) Y. Takeuchi, A. Matsuda, N. Kobayashi, *J. Am. Chem. Soc.* **2007**, *129*8271–8281; d) S. Saito, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2007**, *46*, 5591–5593.

[4] a) N. Kobayashi, R. Kondo, S. Nakajima, T. Osa, *J. Am. Chem. Soc.* **1990**, *112*, 9640–9641; b) N. Kobayashi, T. Ishizaki, K. Ishii, H. Konami, *J. Am. Chem. Soc.* **1999**, *121*, 9096–9110; c) C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835–854; d) T. Fukuda, M. M. Olmstead, W. S. Durfee, N. Kobayashi, *Chem. Commun.* **2003**, 1256–1257; e) T. Torres, *Angew. Chem. Int. Ed.* **2006**, *45*, 2834–2837; f) F. Pichierri, *Chem. Phys. Lett.* **2006**, *426*, 410–414.

[5] a) A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2000**, 1701–1710; b) A. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267–1300; c) S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819–3867; d) P. Ceroni, G. Bergamini, F. Marchioni, V. Balzani, *Prog. Polym. Sci.* **2005**, *30*, 453–473.

[6] a) C. Devadoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 9635–9644; b) D. L. Jiang, T. Aida, *Nature* **1997**, *388*, 454–456; c) M. Kawa, J. M. J. Fréchet, *Chem. Mater.* **1998**, *10*, 286–296; d) F. Vögtle, M,. Plevoets, M. Nieger, G. C. Azzellini, A. Credi, L. De Cola, V. D. Marchis, M. Venturi, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 6290–6298; e) A. Herrmann, T. Weil, V. Sinigersky, U. M. Wiesler, T. Vosch, J. Hofkens, F. C. De Schryver, K. Müllen, *Chem. Eur. J.* **2001**, *7*, 4844–4853; f) T. H. Ghaddar, J. F. Wishart, D. W. Thompson, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2002**, *124*, 8285–8289; g) N. D. McClenaghan, R. Passalacqua, F. Loiseau, S. Campagna, B. Verheyde, A. Hameurlaine, W. Dehaen, *J. Am. Chem. Soc.* **2003**, *125*, 5356–5365; h) M. Gutierrez-Nava, G. Accorsi, P. Masson, N. Armaroli, J. F. Nierengarten, *Chem. Eur. J.* **2004**, *10*, 5076–5086; i) H. John, R. Bauer, P. Espindola, P. Sonar, J. Heinze, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 2447–2451; j) E. V. Andreitchenko, C. G. Clark, J. R. E. Bauer, G. Lieser, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 6348–6354; k) U. Hahn, E. Maisonhaute, C. Amatore, J. F. Nierengarten, *Angew. Chem. Int. Ed.* **2007**, *46*, 951–954; l) C.-Q. Ma, E. Mena-Osteritz, T. Debaerdemaeker, M. M. Wienk, R. A. J. Janssen, P. Bäuerle, *Angew. Chem. Int. Ed.* **2007**, *46*, 1679–1683.

[7] a) F. Würthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port, H. C. Wolf, *J. Am. Chem. Soc.* **1995**, *117*, 8090–8099; b) D. Jiang, T. Aida, *J. Am. Chem. Soc.* **1998**, *120*, 10895–10901; c) J. N. G. Pillow, M. Halim, J. M. Lupton, P. l. Burn, I. D. W. Samuel, *Macromolecules* **1999**, *32*, 5985–5993; d) M. Kimura, T. Shiba, M. Yamazaki, K. Hanabusa, H. Shirai, N. Kobayashi, *J. Am. Chem. Soc.* **2001**, *123*, 5636–5642; e) J. M. Srin, D. W. Brousmiche, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2002**, *124*, 11848–11849; f) K. Onitsuka, H. Kitajima, M. Fujimoto, A. Iuchi, F. Takei, S. Takahashi, *Chem. Commun.* **2002**, 2576–2577; g) T. Imaoka, H. Horiguchi, K. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 340–341; h) B. S. Li, J. Li, Y. Q. Fu, Z. S. Bo, *J. Am. Chem. Soc.* **2004**, *126*, 3430–3431; i) X. Z. Yan, T. Goodson, T. Imaoka, K. Yamamoto, *J. Phys. Chem. B* **2005**, *109*, 9321–9329; j) R. P. Brinas, T. Troxler, R. M. Hochstrasser, S. A. Vinogradov, *J. Am. Chem. Soc.* **2005**, *127*, 11851–11862; k) F. Loiseau, S. Campagna, A. Hameurlaine, W. Dehaen, *J. Am. Chem. Soc.* **2005**, *127*, 11352–11363; l) M. Kozaki, K. Akita, K. Okada, *Org. Lett.* **2007**, *9*, 1509–1512.

[8] a) Z. Zhu, J. S. Moore, *J. Org. Chem.* **2000**, *63*, 116–123; b) A. Hameurlaine, W. Dehaen, *Tetrahedron Lett.* **2003**, *44*, 957–959; c) A. Kimoto, J. S. Cho, M. Higuchi, K. Yamamoto, *Macromolecules* **2004**, *37*, 5531–5537.

[9] a) J. F. Ambrose, R. F. Nelson, *J. Electrochem. Soc.* **1968**, *115*, 1159–1164; b) J. F. Ambrose, L. L. Carpenter, R. F. Nelson, *J. Electrochem. Soc.* **1975**, *122*, 876–894.

[10] a) T. Xu, R. Lu, M. Jin, X. Qiu, P. Xue, C. Bao, Y. Zhao, *Tetrahedron Lett.* **2005**, *46*, 6883–6886; b) T. Xu, R. Lu, X. Qiu, X. Liu, P. Xue, C. Tan, C. Bao, Y. Zhao, *Eur. J. Org. Chem.* **2006**, 4014–4020; c) T. Xu, R. Lu, X. Liu, X. Zheng, X. Qiu, Y. Zhao, *Org. Lett.* **2007**, *9*, 797–800.

[11] F. A. Neugebauer, H. Fisher, *Chem. Ber.* **1972**, *105*, 2686–2693.

[12] a) B. Györi, J. Emri, P. Szarvas, *Acta Chim. (Budapest)* **1975**, *86*, 235–248; b) P. Szarvas, B. Györi, J. Emri, *Acta Chim. (Budapest)* **1971**, *70*, 1–8.

[13] J. S. Lindsey, I. C. Schreyman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827–836.

[14] L. Stryer, R. P. Haugland, *Proc. Natl. Acad. Sci. USA* **1967**, *58*, 719–726.

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