DOI: 10.1002/ejoc.200800646

Subporphyrins with Monodisperse Oligocarbazole Arms

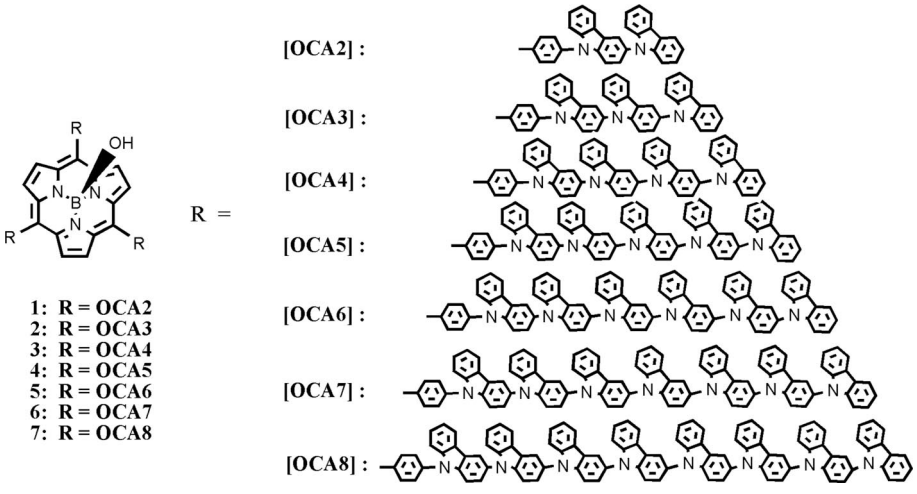
Xingliang Liu,[a] Ran Lu,*[a] Tinghua Xu,[a] Defang Xu,[a] Yong Zhan,[a] Peng Chen,[a] Xianping Qiu,[a] and Yingying Zhao[a]

Keywords: Porphyrinoids / Fluorescence / Conjugation / UV/Vis spectroscopy / Energy transfer

Novel star-shaped subporphyrins with monodisperse oligocarbazole arms were prepared by using pyridine-tri-*N*-pyrrolylborane as a template. It was found that photoinduced energy transfer took place from the oligocarbazole arms to the subporphyrin core, and the energy transfer efficiency decreased with an increase in the number of carbazole units in the arms. These subporphyrins could emit intense yellow-green light when they were excited at 295 nm.

Introduction

As important members in porphyrin families,[1] expanded porphyrins with more than 18π electron have been extensively studied for many years because of their unique properties and potential applications in two-photon absorption, multiple metal ion coordination, and switches.[2–4] Boron-stable azaporphyrins, such as subphthalocyanines (SubPcs), were discovered in 1972 by Meller and Ossko;[5] however, less synthetic effort has been devoted to the preparation of ring-contracted porphyrins. It is known that SubPcs with a cone-shaped conformation comprise 14π-electron systems and their optoelectronic properties can be finetuned by varying the axial ligands or by functionalizing the peripheral substituents.[6] The applications of SubPcs in dye-based technological devices,[7] supramolecular building blocks,[8] and nonlinear optical chromophores[9] have been widely developed. Recently, the first subporphyrin (SubP) with similar electronic structure to SubPc was prepared by the group of Osuka under harsh reaction conditions.[10] Subsequently, more versatile and facile synthetic methods for *meso*-aryl subporphyrins were developed by the groups of Osuka and Kobayashi.[11] Subporphyrins also adopt a nonplanar cone-shaped conformation, and they may serve as a model to understand π-conjugated C_3-symmetric porphyrin systems when three identical groups are introduced into its *meso* positions. Until now, only few subporphyrins bearing pyridyl or phenyl as the substituents in the *meso* positions have been reported.[10,11] It is still a great challenge to synthesize novel subporphyrins modified by func-



Scheme 1. Molecular structures of T(OCA*n*)SubPs **1**–**7**.

[a] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China
Fax: +86-431-88923907
E-mail: luran@mail.jlu.edu.cn
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

tional moieties that realize fascinating optoelectronic properties. It is well known that monodisperse linearly conjugated oligomers bearing well-defined and uniform structures not only represent an ideal model for molecular wires, but also favor tuning their bandgaps to investigate structure–activity relationships. Nowadays, linear π-conjugated oligomers are of great interest in materials science[12] due to their potential applications in the fields of molecular electronics as well as in light-harvesting molecular antenna-type architectures.[13–16] In addition, carbazole-based oligomers are attractive on account of their applications in photoconductors, charge-transporting and emitting materials in OLEDs.[17,18] To the best of our knowledge, there is only one report on a subporphyrin containing linear π-conjugated moieties in the literature.[11g] We recently reported the synthesis of new subporphyrins functionalized with dendritic carbazole arms.[19] Herein, we have designed and synthesized a series of well-defined star-shaped subporphyrins T(OCA*n*)SubPs **1**–**7** with three monodisperse oligocarbazole arms in the *meso* positions (Scheme 1) and investigated their photophysical properties.

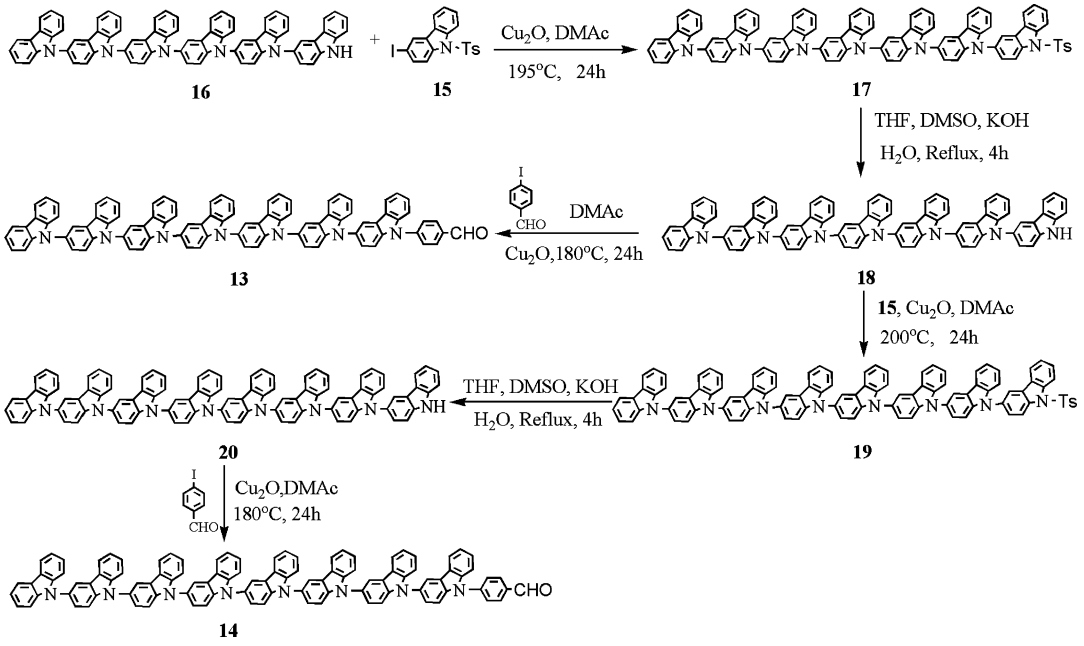
Results and Discussion

Synthesis of the Precursors of the Aldehydes

Oligocarbazole aldehydes **8**–**12** and carbazole hexamer **16** were prepared according to the procedures reported by our group.[20] The synthetic routes for the precursors of oligocarbazole aldehydes **13** and **14** are outlined in Scheme 2. Compound **13** was obtained in a yield of 76% by an Ullmann coupling reaction between *p*-iodobenzaldehyde and **18**, which was prepared by the hydrolysis of compound **17** in a mixture of DMSO, THF, and KOH/H_2O with a good yield of 90%.[21] Compound **17** was synthesized in 76% yield through an Ullmann coupling reaction between 3-iodo-9-tosylcarbazole (**15**) and **16**. Similarly, the Ullmann coupling reaction between *p*-iodobenzaldehyde and **20** could afford aldehyde **14**, and compound **20** was obtained from compound **15** and compound **18** under Ullmann reaction condition, followed by removal of the Ts group.

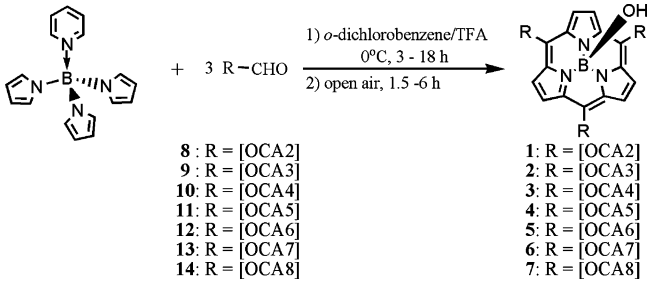
Synthesis of the Subporphyrins

Although tripyrrolylborane may be a promising template for the synthesis of *meso*-aryl-substituted subporphyrins,[11a] it was sensitive to oxygen and moisture, which makes the manipulation become discommodious. Fortunately, Osuka et al. presented another strategy for the synthesis of subporphyrins that involved a one-pot, two-step reaction under milder conditions by using pyridine-tri-*N*-pyrrolylborane, which was stable towards oxygen and moisture, as the template.[11b] Accordingly, we prepared star-shaped subporphyrins **1**–**7** with three monodisperse oligocarbazole arms through the one-pot, two-step reaction as shown in Scheme 3. Firstly, pyridine-tri-*N*-pyrrolylborane and a three molar amount of aldehyde **8** were condensed in the presence of trifluoroacetic acid (TFA) in *o*-dichlorobenzene at 0 °C under an atmosphere of nitrogen for 3 h to avoid acid-promoted scrambling. After the reaction was quenched with pyridine, the mixture was heated to reflux for 1.5 h to complete the air oxidation. The crude product was purified by column chromatography twice to give subporphyrin **1** in a yield of 4.9%. The synthetic methods for subporphyrins **2**–**7** were similar to that of **1**. Because the



Scheme 2. Synthesis of the precursors of aldehydes **13** and **14**.

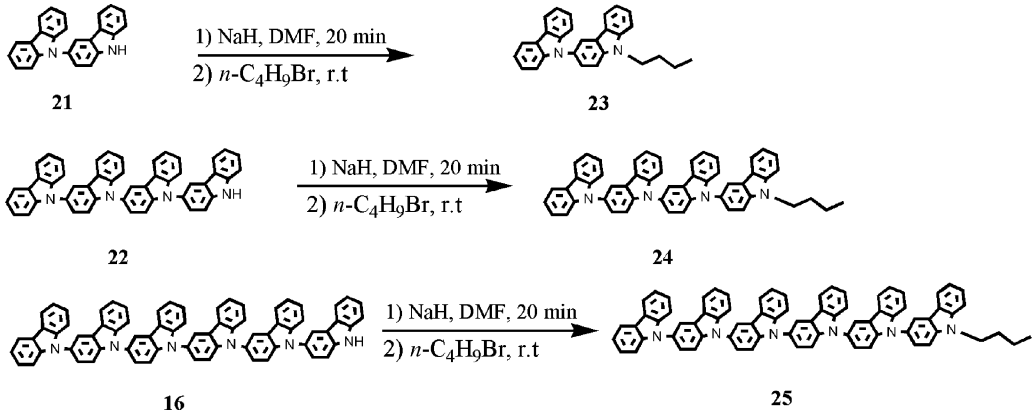
volumes of aldehydes **9**–**14** increased as the number of carbazole units increased, the condensation reaction time was prolonged from 4 to 18 h. To avoid adsorption of the subporphyrins on silica gel, as little as possible silica gel was used during column chromatography. Possessing a similar R_f value with its precursor **13**, compound **6** was obtained after chromatography followed by washing with ethyl acetate owing to its lower solubility in ethyl acetate relative to that of **13**. The purification of subporphyrin **7** was similar to that of **6**. The yields of subporphyrins **2**–**7** were 4.3, 4.0, 3.0, 2.5, 2.2, and 1.8%, respectively. Interestingly, these obtained star-shaped subporphyrins **1**–**7** bear no alkyl groups, but they were well soluble in common organic solvents, such as CH_2Cl_2, chloroform, THF, and toluene. The intermediates and the final products were characterized by ^1H and ^{13}C NMR spectroscopy, FTIR spectroscopy, MALDI-TOF mass spectrometry, and C, H, N elemental analyses (See Supporting Information). The purity of T(OCA*n*)-SubPs **1**–**7** was also confirmed by gel permeation chromatography (GPC) with DMF as the eluent. As shown in Figure S1 (Supporting Information), the retention time decreased gradually with an increase in the molecular weight of the compound, from **1** to **7**, and all the peaks were symmetrical. In order to investigate the excitation energy transfer of the subporphyrins, we synthesized three reference compounds **23**–**25** by alkylation reactions from compounds **21**, **22**, and **16**, respectively (Scheme 4).[18b]



Scheme 3. Synthesis of T(OCA*n*)SubPs **1**–**7**.

Optical Properties of T(OCA*n*)SubPs

The UV/Vis absorption spectra of **1**–**7** in $CHCl_3$ are shown in Figure 1. Several absorption bands were observed in the visible region, including two Q-bands in the range of 450–530 nm, together with a Soret band at 385 nm, and other bands in the UV region (250–350 nm, Table 1) due to the carbazole units. The absorption of the carbazole units was clearly proportional to their increasing number in each star-shaped subporphyrin, which indirectly reflected the flawless or perfect structures of the as-synthesized subporphyrins. In comparison to the *meso*-triphenylsubporphyrin, the Soret bands of the monodisperse oligocarbazole-functionalized subporphyrins **1**–**7** are redshifted from 374 to 385 nm, which might be due to the extensive conjugation in **1**–**7**. From Figure 1b of the fluorescence emission spectra of **1**–**7** in dilute solutions, we can find strong emission bands at ca. 537 nm attributable to the emission of subporphyrin cores and weak emissions due to carbazole units in the range of 350–480 nm under excitation at 295 nm, which can selectively excite the carbazole moieties instead of the subporphyrin core. This indicates that intramolecular energy transfer from the carbazole arms to the subporphyrin cores might take place. The remarkable changes of the time-resolved fluorescence spectra of the subporphyrins compared with the reference compounds (oligocarbazoles) could also confirm the occurrence of the excitation energy transfer in the subporphyrins (Figure S2–S7, Supporting Information). The fluorescence lifetimes of subporphyrins **1**, **3**, and **5** and the reference compounds **21**–**23** were measured in $CHCl_3$ by using a time-correlated single-photon counting (TCSPC) instrument. The fluorescence decay was monitored at 400 nm for the reference compounds, and monitored at 400 and 537 nm for the subporphyrins under excitation at 295 nm. The values of the fluorescence lifetime are given in Table 2. As can be inferred from these data, the lifetimes of the reference compounds decreased with an increase in the number of carbazole units, indicating appearance of a competing nonradiative process in the larger molecules.[22b] Nevertheless, we were unable to measure the lifetime of the subporphyrins in the emission band of the oligocarbazole



Scheme 4. Synthesis of reference compounds **23**–**25**.

arms (400 nm), because the residual emission was too weak to measure with our instrument.[22b] The lifetimes of subporphyrins **1**, **3**, and **5** were measured by monitoring the emission at 537 nm when excited at 295 nm and values of 2.98, 2.80, and 2.45 ns were found. Therefore, it further illustrated the occurrence of the excitation energy transfer from the oligocarbazole arms to the subporphyrin core in star-shape subporphyrins **1**–**7**. Comparison between the excitation and the absorption spectra allowed quantitation of the energy transfer efficiency (Φ_{ET}),[22] and the Φ_{ET} values of **1**–**7** were estimated to be 87, 86, 82, 74, 67, 59, and 55%, respectively (Figures S8–S14, Supporting Information; Table 1). It was clear that the value of Φ_{ET} decreased as the number of carbazole units in the arms increased. On the one hand, there was leveling-off appearance between the energy transfer distance and the light-harvesting ability. In other words, the increased molecular length allowed higher light-harvesting ability due to more light-collecting units (carbazoles); however, it resulted in a larger donor–acceptor separation, which reduced the energy transfer efficiency. On the other hand, the larger molecules favored the occurrence of little vibrational deactivation, which might lead to a decrease in the fluorescence quantum yields to a certain degree.[23] We found that the fluorescence quantum yields of reference compounds **23**–**25** decreased with an increase in the number of carbazoles (Table 2). Thus, the little vibrational deactivation of the oligocarbazole arms was another possible factor to depress the energy transfer efficiency in subporphyrins. In addition, subporphyrins **1**–**7** could emit strong yellow-green light (Figure 2). The fluorescence quantum yields (Φ_F) of **1**–**7** in THF were measured by using quinine sulfate (Φ_F = 0.546) as a standard, and they were 0.132, 0.127, 0.153, 0.131, 0.141, 0.142, and 0.135 (Table 1), respectively.

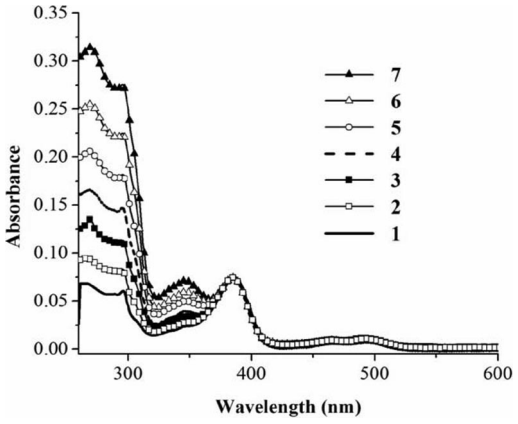


Figure 1. UV/Vis absorption spectra (normalized at the Soret bands) of **1**–**7** in $CHCl_3$.

Table 1. Absorption and fluorescence data for T(OCA*n*)SubPs **1**–**7** in $CHCl_3$.

	λ_{abs}^{max} [nm]	λ_{em}^{max}[a] [nm]	Φ_{ET}[b] [%]	Φ_F[c]
1	295, 346, 385, 466, 494	538	87	0.132
2	295, 346, 385, 466, 494	537	86	0.127
3	295, 346, 385, 466, 494	537	82	0.153
4	295, 346, 385, 466, 494	537	74	0.131
5	295, 346, 385, 466, 494	538	67	0.141
6	295, 346, 385, 466, 494	538	59	0.142
7	295, 346, 385, 466, 494	536	55	0.135

[a] Excited at 295 nm. [b] Energy transfer efficiency (Φ_{ET}) was calculated by comparing the absorption and excitation spectra of T(OCA*n*)SubPs 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_{ex} = 366 nm) as the standard.

Table 2. Fluorescence lifetimes of T(OCA*n*)SubPs **1**, **3**, and **5** and reference compounds **23**–**25**, and the fluorescence quantum yields of compounds **23**–**25**.

	τ[a] [ns]		τ[a] [ns]	Φ_F[b]
T(OCA2)SubP (**1**)	2.98	Compound **23**	1.94	0.218
T(OCA4)SubP (**3**)	2.80	Compound **24**	1.90	0.210
T(OCA6)SubP (**5**)	2.45	Compound **25**	1.85	0.210

[a] Decay profiles were satisfactorily fitted by a single exponential function. [b] The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 (Φ_F = 0.546, λ_{ex} = 366 nm) as the standard.

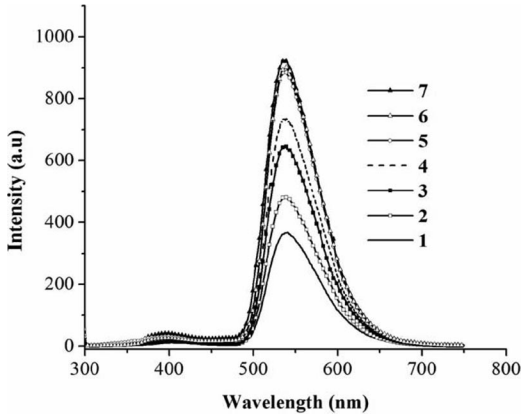


Figure 2. Emission spectra of **1**–**7** at 1 μM in $CHCl_3$ (λ_{ex} = 295 nm).

Conclusions

Novel star-shaped subporphyrins functionalized with three monodisperse oligocarbazole arms T(OCA*n*)SubPs (**1**–**7**) were synthesized through one-pot, two-step reactions from pyridine-tri-*N*-pyrrolylborane and the corresponding aldehydes. Such facile synthetic methodology is helpful for us to construct other functional subporphyrins with desired properties. The photophysical investigation indicates an efficient energy transfer occurs from the oligocarbazole arms to the subporphyrin core, and the efficiency of the energy transfer decreases with an increase in the number of carbazole units in accordance with Förster energy transfer mechanism. In addition, the as-synthesized subporphyrins emit intense yellow-green light. Such novel subporphyrins might be good candidates for optical materials.

Experimental Section

General: 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. Compounds **13**, **14**, and **16**–**22** were synthesized according to the procedures reported by our group.[20] Tri-*N*-pyrrolylborane was prepared from $LiBH_4$ and pyrrole by a reported procedure and was converted into pyridine-tri-*N*-pyrrolylborane by treatment with dry pyridine under an atmosphere of nitrogen. ^1H and ^{13}C NMR spectra were recorded with a Mercury plus instrument at 500 and 125 MHz by using $CDCl_3$ as the solvent in all cases. UV/Vis spectra were determined with a Shimadzu UV-1601PC spectrophotometer. Photoluminescence (PL) spectra were carried out with a Shimadzu RF-5301 luminescence spectrometer. IR spectra were measured by using a Nicolet-360 FTIR spectrometer by incorporating samples in KBr disks. Mass spectra were performed with Agilent 1100 MS series and AXIMA CFR MALDI/TOF (matrix-assisted laser desorption ionization/time-of-flight) MS (COMPACT). C, H, and N elemental analyses were taken with a Perkin–Elmer 240C elemental analyzer. The gel permeation chromatography (GPC) measurements were performed with a Waters chromatograph connected to a Waters 410 differential refractometer with DMF as eluent.

3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9-(9-tosyl-9*H*-carbazol-6-yl)-9*H*-carbazole (17): Compound **16** (8.48 g, 8.5 mmol), 3-iodo-9-tosylcarbazole (**15**; 5.7 g, 13 mmol), Cu_2O (3.5 g, 24 mmol), and DMAc (20 mL) were added sequentially into a seal tube under a nitrogen atmosphere and heated to 195 °C in an oil bath for 24 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 crude product was collected by filtration and recrystallized from EtOH/THF (3:2) to give **17** (8.5 g, 76%) as a white solid. M.p. >250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 8.5 Hz, 1 H), 8.42 (d, J = 8.5 Hz, 5 H), 8.32 (s, 1 H), 8.22–8.15 (m, 8 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.86 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 9.0 Hz, 1 H), 7.65–7.60 (m, 9 H), 7.56–7.43 (m, 17 H), 7.40–7.30 (m, 7 H), 7.23 (d, J = 8.0 Hz, 2 H), 2.35 (s, 3 H, -CH_3) ppm. $C_{91}H_{57}N_7O_2S$ (1312.54): calcd. C 83.27, H 4.38, N 7.47; found C 83.40, H 4.63, N 7.38.

3-{3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazole (18): To a solution of compound **17** (9.2 g, 7.0 mmol) dissolved in THF (34 mL), DMSO (17 mL), and H_2O (7 mL) was added KOH (7.0 g, 0.13 mol). The mixture was heated at reflux for 4 h (monitored by TLC), cooled to room temperature, neutralized by HCl, and then poured into water to give a white solid. The crude product was purified on silica gel (petroleum ether/CH_2Cl_2, 3:1) to afford **18** (7.3 g, 90%) as a white solid. M.p. >250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.42–8.41 (m, 4 H), 8.32–8.29 (m, 2 H), 8.21–8.09 (m, 8 H), 7.68–7.63 (m, 11 H), 7.51–7.36 (m, 18 H), 7.35–7.29 (m, 8 H) ppm. MS (MALDI-TOF): m/z = 1157.7. $C_{84}H_{51}N_7$ (1158.35): calcd. C 87.10, H 4.44, N 8.46; found C 87.33, H 4.54, N 8.53.

4-(3-{3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)benzaldehyde (13): Compound **18** (7.0 g, 6.0 mmol), 4-iodobenzaldehyde (4.0 g, 17 mmol), Cu_2O (2.5 g, 17 mmol), and DMAc (20 mL) were added sequentially into a seal tube under a nitrogen atmosphere and heated to 180 °C in oil bath for 18 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 crude product was collected by filtration, and purified by chromatography (silica gel; petroleum ether/CH_2Cl_2, 1:3) and then recrystallized from EtOH/THF (3:2) to give **13** (5.4 g, 71%) as a light-yellow solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 1701.0 [s, ν_s(C=O)] cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 10.17 (s, 1 H, -CHO), 8.42 (d, J = 12.0 Hz, 4 H), 8.32 (s, 1 H), 8.23–8.16 (m, 9 H), 7.91 (d, J = 8.5 Hz, 2 H), 7.77–7.61 (m, 14 H), 7.60–7.43 (m, 12 H), 7.42–7.30 (m, 12 H) ppm. MS (MALDI-TOF): m/z = 1261.8. $C_{91}H_{55}N_7O$ (1262.46): calcd. C 86.58, H 4.39, N 7.77; found C 86.42, H 4.63, N 7.96.

3-{3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9-(9-tosyl-9*H*-carbazol-6-yl)-9*H*-carbazole (19): By following the synthetic procedure for compound **17** and by using compound **18** (7.9 g, 6.8 mmol), **15** (4.5 g, 10 mmol), Cu_2O (2.5 g, 17 mmol), and DMAc (20 mL) as reagents, the Ullmann reaction was carried out at 200 °C in an oil bath for 28 h. The crude product was recrystallized from EtOH/THF (3:2) to give **19** (8.0 g, 79%) as a white solid. M.p. >250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 8.5 Hz, 1 H), 8.43 (d, J = 9.5 Hz, 6 H), 8.33 (s, 1 H), 8.23–8.15 (m, 9 H), 7.96 (d, J = 7.5 Hz, 1 H), 7.87 (d, J = 8.5 Hz, 2 H), 7.79–7.77 (m, 1 H), 7.66–7.65 (m, 12 H), 7.52–7.48 (m, 13 H), 7.44–7.30 (m, 13 H), 7.24 (d, J = 8.0 Hz, 2 H), 2.35 (s, 3 H) ppm. $C_{103}H_{64}N_8O_2S$ (1477.73): calcd. C 83.72, H 4.37, N 7.58; found C 83.71, H 4.30, N 7.68.

3-{3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9-(9H-carbazol-6-yl)-9*H*-carbazole (20): By following the synthetic procedure for compound **18**, compound **20** (8.3 g, 5.6 mmol) was hydrolyzed in THF (52 mL), DMSO (26 mL), and H_2O (10 mL) containing KOH (7.0 g, 0.13 mol), and **20** (6.6 g, 89%) was obtained as a white solid after chromatography (silica gel; petroleum ether/CH_2Cl_2, 1:2). M.p. >250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.42–8.40 (m, 5 H), 8.32 (s, 2 H), 8.21–8.09 (m, 9 H), 8.03 (s, 1 H), 7.66–7.62 (m, 13 H), 7.51–7.42 (m, 19 H), 7.36–7.29 (m, 9 H) ppm. MS (MALDI-TOF): m/z = 1323.1. $C_{96}H_{58}N_8$ (1323.54): calcd. C 87.12, H 4.42, N 8.47; found C 87.09, H 4.67, N 8.50.

4-[3-(3-{3-[3-(3-{3-[3-(9H-Carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]-9*H*-carbazol-9-yl}-9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl]benzaldehyde (14): By following the synthetic procedure for compound **13** and by using compound **20** (6.5 g, 4.9 mmol), 4-iodobenzaldehyde (3.0 g, 13 mmol), Cu_2O (2.5 g, 17 mmol), and DMAc (20 mL) as solvents, the Ullmann reaction was carried out at 180 °C in an oil bath for 18 h. The crude product was purified by chromatography (silica gel; petroleum ether/CH_2Cl, 1:3) and then recrystallized from EtOH/THF (1:1) to give **14** (5.2 g, 74%) as a light-yellow solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 1700.1 [s, ν_s(C=O)] cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 10.17 (s, 1 H, -CHO), 8.42 (d, J = 13.0 Hz, 5 H), 8.32 (s, 1 H), 8.23–8.15 (m, 10 H), 7.91 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 9.0 Hz, 1 H), 7.70–7.58 (m, 13 H), 7.55–7.49 (m, 14 H), 7.43–7.36 (m, 12 H), 7.30–7.28 (m, 3 H) ppm. MS (MALDI-TOF): m/z = 1426.9. $C_{103}H_{62}N_8O$ (1427.65): calcd. C 86.65, H 4.38, N 7.85; found C 86.59, H 4.44, N 7.81.

9-(9-Butyl-9*H*-carbazol-3-yl)-9*H*-carbazole (23): To a solution of compound **21** (1.4 g, 4.3 mmol) in DMF (30 mL) was added NaH (60 wt.-%, 0.25 g, 6.3 mmol) and *n*-C_4H_9Br (4.6 mL, 4.3 mmol). The mixture was stirred at room temperature until the reaction was complete, as monitored by TLC. The mixture was poured into water (200 mL), and the precipitate was collected by filtration and recrystallized from petroleum ether to give **23** (1.5 g, 90%) as a white solid. M.p. 144.0–146.0 °C. ^1H NMR (500 MHz, $CDCl_3$): δ

= 8.22 (s, 1 H), 8.17 (d, *J* = 8.0 Hz, 2 H), 8.04 (d, *J* = 5.5 Hz, 1 H), 7.56 (s, 2 H), 7.50–7.45 (m, 2 H), 7.41–7.38 (m, 4 H), 7.29–7.27 (m, 2 H), 7.25–7.21 (m, 1 H), 4.37–4.34 (m, 2 H), 1.95–1.89 (m, 2 H), 1.49–1.44 (m, 2 H), 1.01–0.98 (t, 3 H) ppm.

9-{9-[9-(9-Butyl-9*H*-carbazol-3-yl)-9*H*-carbazol-3-yl]-9*H*-carbazol-3-yl}-9*H*-carbazole (24): The synthesis of compound **24** from **22** was similar to that of **23** from **21**. After purification by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1), **24** (2.6 g, 85%) was obtained as a white solid. M.p. 214.0–216.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (s, 1 H), 8.33–8.32 (m, 2 H), 8.19–8.10 (m, 5 H), 7.67–7.59 (m, 5 H), 7.55–7.41 (m, 11 H), 7.34–7.28 (m, 5 H), 4.44–4.41 (m, 2 H), 2.00–1.95 (m, 2 H), 1.51–1.48 (m, 2 H), 1.04–1.01 (t, 3 H) ppm.

9-[9-(9-{9-[9-(9-Butyl-9*H*-carbazol-3-yl)-9*H*-carbazol-3-yl]-9*H*-carbazol-3-yl}-9*H*-carbazol-3-yl)-9*H*-carbazol-3-yl]-9*H*-carbazole (25): The synthesis of compound **25** from **16** was similar to that of **23** from **21**. After purification by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1), **25** (3.8 g, 82%) was obtained as a white solid. M.p. >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42–8.40 (m, 3 H), 8.33 (d, *J* = 8.5 Hz, 2 H), 8.20–8.10 (m, 7 H), 7.67–7.62 (m, 9 H), 7.54–7.42 (m, 15 H), 7.36–7.28 (m, 7 H), 4.44–4.42 (m, 2 H), 1.99–1.96 (m, 2 H), 1.53–1.48 (m, 2 H), 1.04–1.01 (t, 3 H) ppm.

T(OCA2)SubP (1): To a suspension of pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) in *o*-dichlorobenzene (45 mL) was added OCA2-CHO (**8**; 1.4 g, 3.21 mmol), and the mixture was cooled to 0 °C in an ice bath. After adding trifluoroacetic acid (0.085 mL, 1.10 mmol) dropwise by syringe, the mixture immediately turned deep red from light-yellow. After stirring at 0 °C for 3 h under an atmosphere of nitrogen in the dark, the reaction was quenched with pyridine (0.1 mL), and the resulting solution was heated to reflux in the open air for 1.5 h. Black tar was obtained after the solvent was removed by distilling, which was purified by chromatography (silica gel, CH_2Cl_2) twice to give **1** (75 mg, 4.9%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3420 [s, ν_s(OH)] cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.44–8.38 (m, 15 H), 8.22–8.20 (m, 9 H), 8.08 (d, *J* = 8.5 Hz, 6 H), 7.93 (d, *J* = 9.0 Hz, 3 H), 7.81 (d, *J* = 8.0 Hz, 3 H), 7.69–7.67 (m, 3 H), 7.62–7.59 (t, 3 H), 7.48–7.40 (m, 15 H), 7.34–7.31 (t, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8, 141.4, 140.4, 139.8, 137.4, 136.4, 134.6, 130.2, 127.2, 126.9, 125.9, 125.7, 124.7, 123.2, 123.1, 122.7, 120.8, 120.3, 119.6, 111.1, 110.3, 109.8 ppm. MS (MALDI-TOF): *m*/*z* = 1461.3 [M – OH]$^+$. $C_{105}H_{64}BN_9O$ (1478.50): calcd. C 85.30, H 4.36, N 8.53; found C 85.22, H 4.45, N 8.47.

T(OCA3)SubP (2): By following the synthetic procedure for compound **1** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA3-CHO (**9**; 1.9 g, 3.16 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 4 h under an atmosphere of nitrogen in the dark. The subsequent oxidation reaction was carried out in the open air under reflux for 2 h. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice to give **2** (90 mg, 4.3%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3425 [s, ν_s(OH)] cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46–8.42 (m, 12 H), 8.35 (s, 3 H), 8.26–8.17 (m, 12 H), 8.11 (d, *J* = 8.0 Hz, 6 H), 7.98 (d, *J* = 8.5 Hz, 3 H), 7.82 (d, *J* = 8.5 Hz, 3 H), 7.77–7.75 (m, 3 H), 7.66–7.57 (m, 12 H), 7.52–7.51 (m, 6 H), 7.47–7.43 (m, 15 H), 7.36–7.31 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 141.9, 141.5, 141.0, 140.4, 140.0, 137.4, 136.5, 134.6, 129.9, 129.6, 127.2, 127.0, 126.6, 125.8, 125.6, 125.5, 124.8, 124.1, 123.2, 123.0, 122.8, 122.7, 120.9, 120.6, 120.3, 120.1, 119.7, 119.6, 119.5, 111.2, 110.9, 110.4, 110.2, 109.8 ppm. MS (MALDI-TOF): *m*/*z* = 1956.6 [M – OH]$^+$. $C_{141}H_{85}BN_{12}O$ (1974.07): calcd. C 85.79, H 4.34, N 8.51; found C 86.04, H 4.42, N 8.27.

T(OCA4)SubP (3): By following the synthetic procedure for compound **2** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA4-CHO (**10**; 2.4 g, 3.13 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 6 h under an atmosphere of nitrogen in the dark. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice to give **3** (103 mg, 4.0%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3420 [s, ν_s(OH)] cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48–8.42 (m, 15 H), 8.33 (s, 3 H), 8.27–8.10 (m, 21 H), 8.00 (d, *J* = 8.5 Hz, 3 H), 7.83–7.77 (m, 6 H), 7.70–7.61 (m, 12 H), 7.56–7.50 (m, 15 H), 7.46–7.38 (m, 21 H), 7.34–7.28 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.6, 141.9, 141.6, 141.2, 141.1, 140.5, 140.1, 137.4, 136.6, 134.7, 129.8, 129.5, 129.3, 127.3, 127.1, 126.8, 126.6, 125.8, 125.6, 125.4, 124.9, 124.2, 124.0, 123.2, 123.1, 122.8, 122.7, 120.9, 120.7, 120.6, 120.3, 120.0, 119.7, 119.6, 119.5, 111.3, 111.0, 110.9, 110.3, 109.8 ppm. MS (MALDI-TOF): *m*/*z* = 2451.8 [M – OH]$^+$. $C_{177}H_{106}BN_{15}O$ (2469.65): calcd. C 86.08, H 4.33, N 8.51; found C 86.11, H 4.40, N 8.62.

T(OCA5)SubP (4): By following the synthetic procedure for compound **1** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA5-CHO (**11**; 2.9 g, 3.11 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 8 h under an atmosphere of nitrogen in the dark. The subsequent oxidation reaction was carried out in the open air under reflux for 2.5 h. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice to give **4** (92 mg, 3.0%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3430 [s, ν_s(OH)] cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.49–8.42 (m, 15 H), 8.32 (s, 3 H), 8.28–8.11 (m, 24 H), 8.00 (d, *J* = 8.0 Hz, 3 H), 7.84–7.77 (m, 6 H), 7.72–7.60 (m, 21 H), 7.54–7.42 (m, 48 H), 7.29 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.7, 142.0, 141.6, 141.3, 141.1, 140.5, 137.5, 136.6, 134.6, 129.9, 129.6, 129.2, 127.3, 127.1, 126.8, 126.7, 126.5, 125.8, 125.6, 125.4, 124.9, 124.3, 124.2, 124.0, 123.2, 123.1, 122.7, 120.9, 120.8, 120.6, 120.2, 120.0, 119.6, 119.5, 111.1, 110.9, 110.3, 109.8 ppm. MS (MALDI-TOF): *m*/*z* = 2946.8 [M – OH]$^+$. $C_{213}H_{127}BN_{18}O$ (2965.22): calcd. C 86.28, H 4.32, N 8.50; found C 86.18, H 4.41, N 8.43.

T(OCA6)SubP (5): By following the synthetic procedure for compound **1** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA6-CHO (**12**; 3.5 g, 3.20 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 11 h under an atmosphere of nitrogen in the dark. The subsequent oxidation reaction was carried out in the open air under reflux for 3.5 h. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice to give **5** (92 mg, 2.5%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3430 [s, ν_s(OH)] cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48–8.40 (m, 21 H), 8.31 (s, 3 H), 8.27–8.10 (m, 27 H), 8.00 (d, *J* = 8.5 Hz, 3 H), 7.83–7.77 (m, 6 H), 7.70–7.61 (m, 24 H), 7.55–7.48 (m, 30 H), 7.42–7.28 (m, 33 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8, 142.7, 142.0, 141.7, 141.4, 141.2, 140.6, 140.2, 137.5, 136.7, 134.7, 129.9, 129.6, 129.3, 127.3, 127.1, 126.7, 126.6, 125.8, 125.6, 125.5, 125.0, 124.3, 124.2, 124.1, 123.3, 123.1, 122.7, 121.0, 120.9, 120.6, 120.3, 120.2, 120.0, 119.5, 111.2, 111.0, 110.4, 109.9 ppm. MS (MALDI-TOF): *m*/*z* = 3441.2 [M – OH]$^+$. $C_{249}H_{148}BN_{21}O$ (3460.79): calcd. C 86.42, H 4.31, N 8.50; found C 86.47, H 4.38, N 8.47.

T(OCA7)SubP (6): By following the synthetic procedure for compound **1** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA7-CHO (**13**; 3.9 g, 3.09 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 14 h

under an atmosphere of nitrogen in the dark. The subsequent oxidation reaction was carried out in the open air under reflux for 5 h. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice and washed with ethyl acetate to give **6** (92 mg, 2.2%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3415 [s, ν_s(OH)] cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.48–8.40 (m, 21 H), 8.31 (s, 3 H), 8.25–8.10 (m, 30 H), 8.00 (d, J = 8.5 Hz, 3 H), 7.83–7.76 (m, 6 H), 7.67–7.59 (m, 30 H), 7.54–7.28 (m, 75 H) ppm. MS (MALDI-TOF): m/z = 3936.2 [M – OH]$^+$. $C_{285}H_{169}BN_{24}O$ (3956.36): calcd. C 86.52, H 4.31, N 8.50; found C 86.39, H 4.41, N 8.32.

T(OCA8)SubP (7): By following the synthetic procedure for compound **1** and by using pyridine-tri-*N*-pyrrolylborane (300 mg, 1.04 mmol) and OCA8-CHO (**14**; 4.5 g, 3.15 mmol) as reagents in *o*-dichlorobenzene (45 mL), the mixture was stirred at 0 °C for 18 h under an atmosphere of nitrogen in the dark. The subsequent oxidation reaction was carried out in the open air under reflux for 6 h. The crude product was purified by chromatography (silica gel, CH_2Cl_2) twice and washed with ethyl acetate to give **7** (83 mg, 1.8%) as a brown-orange solid. M.p. >250 °C. IR (KBr): $\tilde{\nu}$ = 3430 [s, ν_s(OH)] cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.48–8.39 (m, 27 H), 8.31 (s, 3 H), 8.24–8.10 (m, 33 H), 8.00 (d, J = 8.0 Hz, 3 H), 7.83–7.76 (m, 6 H), 7.67–7.65 (m, 36 H), 7.54–7.51 (m, 42 H), 7.42–7.35 (m, 39 H) ppm. MS (MALDI-TOF): m/z = 4433.0 [M – OH]$^+$. $C_{321}H_{190}BN_{27}O$ (4451.93): calcd. C 86.60, H 4.30, N 8.49; found C 86.42, H 4.48, N 8.73.

Supporting Information (see footnote on the first page of this article): GPC traces of **1**–**7**; selected fluorescence decay curves; selected absorption and excitation curves; ^1H and ^{13}C NMR spectra and mass spectrometry data for all new compounds.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (NNSFC, Nos. 20574027 and 20874034), 973 Program (2009CB939701) and the Program for New Century Excellent Talents in University (NCET).

[1] a) B. Franck, A. Nonn, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1795–1811; b) J. L. D. Sessler, D. Scidel, *Angew. Chem. Int. Ed.* **2003**, *42*, 5134–5175.

[2] a) A. Jasat, D. Dolphin, *Chem. Rev.* **1997**, *97*, 2267–2340; b) T. D. Lash, *Angew. Chem. Int. Ed.* **2000**, *39*, 1763–1767; c) A. Ghosh, *Angew. Chem. Int. Ed.* **2004**, *43*, 1918–1931.

[3] a) J. L. Sessler, M. J. Cyr, V. Lynch, E. McGhee, J. A. Ibers, *J. Am. Chem. Soc.* **1990**, *112*, 2810–2813; b) J. L. Sessler, S. J. Weghorn, V. Lynch, M. R. Johnson, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1509–1512; c) J. Sestune, S. Maeda, *J. Am. Chem. Soc.* **2000**, *122*, 12405–12406; d) V. G. Anand, S. K. Pushpan, S. Venkatraman, A. Dey, T. K. Chandrashekar, B. S. Joshi, R. Roy, W. Teng, K. R. Senge, *J. Am. Chem. Soc.* **2001**, *123*, 8620–8621; e) A. Krivokapic, A. R. Cowley, H. L. Anderson, *J. Org. Chem.* **2003**, *68*, 1089–1096; f) L. Xu, G. M. Ferrence, T. D. Lash, *Org. Lett.* **2006**, *8*, 5113–5116.

[4] a) M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* **1999**, 385–386; b) J. Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190–7191; c) M. Suzuki, A. Osuka, *Org. Lett.* **2003**, *5*, 3943–3946; d) S. Shimizu, J. Y. Shin, H. Furuta, R. Ismael, A. Osuka, *Angew. Chem. Int. Ed.* **2003**, *42*, 78–82; e) S. Shimizu, N. Aratani, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 4909–4918.

[5] A. Meller, A. Ossko, *Monatsh. Chem.* **1972**, *103*, 150.

[6] a) C. G. Claessens, D. González-Rodríguez, T. Torres, *Chem. Rev.* **2002**, *102*, 835–854; b) R. S. Iglesias, C. G. Claessens, M. Ángeles Herranz, T. Tomas, *Org. Lett.* **2007**, *9*, 5381–5384.

[7] T. Torres, C. G. Claessens, R. S. Iglesias, D. González-Rodríguez, M. V. Martínez-Díaz, (Universidad Autónoma de Madrid, Spain), Spanish Patent ES 200401615, **2005**.

[8] a) C. G. Claessens, T. Torres, *Chem. Commun.* **2004**, *11*, 1298–1299; b) S. Berner, M. De Wild, L. Ramoino, S. Ivan, A. Baratoff, H.-J. Guentherodt, H. Suzuki, D. Schlettwein, T. A. Jung, *Phys. Rev. B* **2003**, *68*, 115410/1–11541.0/11; c) C. G. Claessens, T. Torres, *J. Am. Chem. Soc.* **2002**, *124*, 14522–14523; d) M. De Wild, S. Berner, H. Suzuki, H. Yanagi, D. Schlettwein, S. Ivan, A. Baratoff, H.-J. Guentherodt, T. A. Jung, *ChemPhysChem* **2002**, *3*, 881–885.

[9] a) C. G. Claessens, D. González-Rodríguez, T. Torres, G. Martín, F. Agulló-López, I. Ledoux, J. Zyss, V. R. Ferro, J. M. de la Vega, *J. Phys. Chem. B* **2005**, *109*, 3800–3806; b) G. Martín, G. Rojo, F. Agulló-López, V. R. Ferro, J. M. García de la Vega, M. V. Martínez-Díaz, T. Torres, I. Ledoux, J. Zyss, *J. Phys. Chem. B* **2002**, *106*, 13139–13145; c) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Marti, S. Brasselet, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **1998**, *120*, 12808–12817.

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

[11] 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) E. Tsurumaki, S. Saito, K. S. Kim, J. M. Lim, Y. Inokuma, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 438–439; e) T. Torres, *Angew. Chem. Int. Ed.* **2006**, *45*, 2834–2837; f) Y. Inokuma, A. Osuka, *Chem. Commun.* **2007**, *28*, 2938–2940; g) Y. Inokuma, S. Easwaramoorthy, S. Y. Jang, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 4840–4843.

[12] a) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537–553; b) R. E. Martin, F. Diederich, *Angew. Chem. Int. Ed.* **1999**, *38*, 1350–1377; c) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; d) A. C. Grimsdale, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5592–5629.

[13] P. F. Van Hutten, J. Wideman, A. Meetsma, G. Hadziioannou, *J. Am. Chem. Soc.* **1999**, *121*, 5910–5918.

[14] a) F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, P. Alnot, *J. Am. Chem. Soc.* **1993**, *115*, 8716–8721; b) H. E. Katz, *J. Mater. Chem.* **1997**, *7*, 369–376.

[15] a) J. F. Eckert, J. F. Nicoud, J. F. Nierengarten, S. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479; b) J. L. D. de la Cruz, U. Hahn, J. F. Nierengarten, *Tetrahedron Lett.* **2006**, *47*, 3715–3718.

[16] a) M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461; b) H. Imahori, Y. Sakata, *Adv. Mater.* **1997**, *9*, 537–546.

[17] a) J.-F. Morin, M. Leclerc, *Macromolecules* **2001**, *34*, 4680–4682; b) A. Kimoto, J. S. Cho, M. Higuchi, K. Yamamoto, *Macromolecules* **2004**, *37*, 5531–5537; c) A. Hameurlaine, W. Dehaen, *Tetrahedron Lett.* **2003**, *44*, 957–959; d) Z. G. Zhu, J. S. Moore, *J. Org. Chem.* **2000**, *65*, 116–123; e) M. Sonntag, P. Strohriegl, *Chem. Mater.* **2004**, *16*, 4736–4742; f) J. F. Morin, M. Leclerc, *Macromolecules* **2002**, *35*, 8413–8417; g) Z. Zhao, X. Xu, H. Wang, P. Lu, G. Yu, Y. Liu, *J. Org. Chem.* **2008**, *73*, 594–602.

[18] 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; d) X. Yang, R. Lu, T. Xu, P. Xue, X. Liu, Y. Zhao, *Chem. Commun.* **2008**, *4*, 453–455.

[19] T. Xu, R. Lu, X. Liu, P. Chen, X. Qiu, Y. Zhao, *Eur. J. Org. Chem.* **2008**, 1065–1071.
[20] T. Xu, R. Lu, X. Liu, P. Chen, X. Qiu, Y. Zhao, *J. Org. Chem.* **2008**, *73*, 1809–1817.
[21] a) A. Kimoto, J. S. Cho, M. Higuchi, K. Yamamoto, *Macromolecules* **2004**, *37*, 5531–5537; b) A. Hameurlaine, W. Dehaen, *Tetrahedron Lett.* **2003**, *44*, 957–959.
[22] a) L. Stryer, R. P. Haugland, *Proc. Natl. Acad. Sci. USA* **1967**, *58*, 719–726; b) C. Devadoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 9635–9644.
[23] J.-F. Nierengarten, S. Zhang, A. Gegout, M. Urbani, N. Armaroli, G. Marconi, Y. Rio, *J. Org. Chem.* **2005**, *70*, 7550–7557.
Received: July 1, 2008
Published Online: November 28, 2008

