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Dendrimers

Polypyrene Dendrimers**

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The aromatic hydrocarbon pyrene is an important and thoroughly investigated organic chromophore. Among the characteristics that make pyrene attractive is its superior ability to form intermolecular excimers[1] in concentrated solution and in the solid state, as well as intramolecular excimers[2] independent of concentration. This excimer formation has been widely used to study the viscosity of micelles, phospholipids and biological membranes.[3–6] Important properties of pyrene include the exceptionally long fluorescence lifetime[1c] and the solvent polarity dependence of the vibrational peak intensities[7] in the fluorescence spectrum.

Substitution in the pyrene ring at the most active centers (1-, 3-, 6-,and 8-positions) exclusively by pyrene units leads to interesting dendritic architectures with a well-defined number of chromophores in a confined volume. At these positions, only 1,1′-bipyrenyl[8] and linear 1,6-disubstituted oligopyrenes[9] have been studied. Pyrene has often been incorporated as the active core of dendrimers to evaluate the degree of site-isolation of the core.[10] The pyrene chromophore has also been attached as the terminal group of dendrimers in order to investigate the interactions between branches, and also energy and electron transfer among the chromophores and between the core and the periphery.[11] Examples of dendrimers including pyrene both at the core and periphery are very rare,[12] and multichromophoric dendrimers consisting exclusively of pyrene units have, to our knowledge, not been reported to date.

Herein, we report the synthesis, characterization and photophysical studies of a new type of dendrimer, polypyrene dendrimers, represented by the first-generation dendrimer **Py(5)**, consisting of five pyrene units, and the second-generation dendrimer **Py(17)**, comprising seventeen pyrene units (Figure 1), as well two model compounds, **Py(2)** and **Py(3)**, consisting of two and three pyrene chromophores, respectively (Figure 2). The large steric hindrance between pyrenes at the 1-position results in a high degree of twisting,

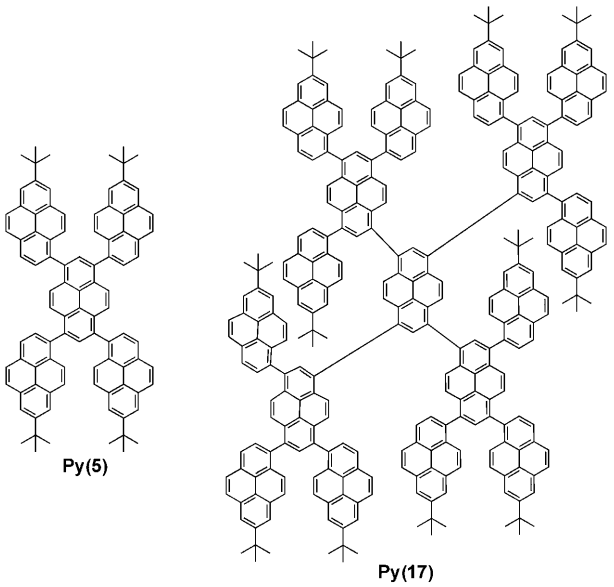

Figure 1. First-generation dendrimer **Py(5)** and second-generation dendrimer **Py(17)**.

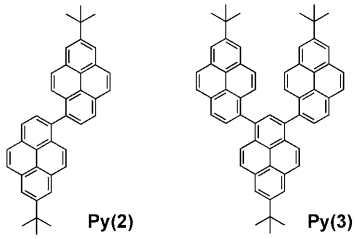

Figure 2. Model compounds **Py(2)** and **Py(3)**.

as shown by the computed structures (AM1, Figure 3). The calculated dihedral angle between the core and the first branch is 65–66° for **Py(5)** and 71–73° for **Py(17)**, with the angle between the first and the second branch in **Py(17)** around 84–89°. These new fully aromatic dendrimers are relevant for artificial light-harvesting in a spatially well-defined three-dimensional architecture, comprising only one type of chromophore. Compared to other stiff aromatic architectures, such as polyphenylene dendrimers,[13] in which several dyes must be attached to the phenylene scaffold to

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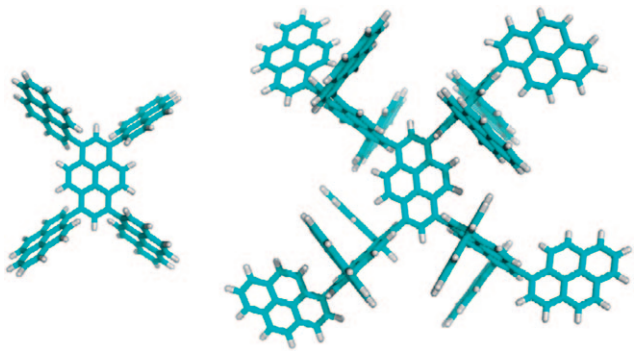
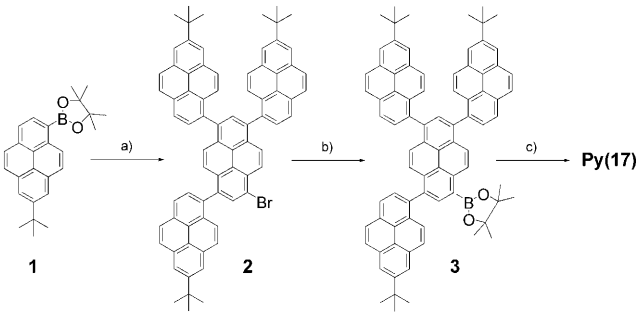


Figure 3. Calculated (AM1) 3D structures of first-generation dendrimer **Py(5)** (left) and second-generation dendrimer **Py(17)** (right).

obtain a multichromophoric shape-persistent structure,[14] each unit in these new systems is already a chromophore. The molecular design was based on the innate reactivity of pyrene, which dictated the 1,3,6,8-substitution pattern. The use of *tert*-butyl groups was strategic in order to disfavor π–π interactions between neighboring molecules and promote solubility.

The synthesis of the first-generation dendrimer **Py(5)** commenced with the preparation of 7-*tert*-butylpyrene-1-boronic acid pinacol ester. Pyrene was selectively mono-*tert*-butylated to afford 2-*tert*-butylpyrene,[15] which was then treated with bromine (1 equivalent) in CH_2Cl_2 at −78 °C, to provide 1-bromo-7-*tert*-butylpyrene in 75 % yield. Borylation under Suzuki–Miyaura conditions[16] using bis(pinacolato)diboron afforded the desired building block in 98 % yield. The Suzuki–Miyaura cross-coupling of 7-*tert*-butylpyrene-1-boronic acid pinacol ester with tetrabromopyrene[10b] using $[Pd(PPh_3)_4]$ as the catalyst and K_2CO_3 as the base in toluene/H_2O at 80 °C afforded the 1,3,6,8-tetrakis(7-*tert*-1-pyrenyl)pyrene **Py(5)** in 42 % yield. The second-generation dendrimer **Py(17)** was synthesized using an approach that can be extended to higher generation dendrimers (Scheme 1). The critical step was the coupling reaction between boronic ester **1** (3.0 equivalents) with 1,3,6,8-tetrabromopyrene. The best results were achieved in the presence of $[Pd(PPh_3)_4]$ and $Ba(OH)_2{\cdot}8H_2O$ as base in toluene at 80 °C, providing bromide



Scheme 1. Synthesis of second-generation dendrimer **Py(17)**. Reagents and conditions: a) 1,3,6,8-tetrabromopyrene, $[Pd(PPh_3)_4]$, $Ba(OH)_2{\cdot}8H_2O$, Aliquat 336, toluene, 80 °C, 20 %; b) bis(pinacolato)diboron, $[Pd(dppf)Cl_2]$, KOAc, 1,4-dioxane, 90 °C, 98 %; c) 1,3,6,8-tetrabromopyrene, $[Pd(PPh_3)_4]$, $Ba(OH)_2{\cdot}8H_2O$, Aliquat 336, toluene, 80 °C, 38 %. dppf = 1,1′-bis(diphenylphosphino)ferrocene.

2 in 20 % yield. Subsequently, bromide **2** was converted into the pinacol boronic ester **3** under Suzuki–Miyaura conditions[16] in 98 % yield. The optimized coupling reaction of compound **3** (6.0 equivalents) with 1,3,6,8-tetrabromopyrene gave a complex mixture of products from which 1,3,6,8-tetrakis(7-*tert*-butylpyren-1-yl)pyrene **Py(17)** was successfully isolated in 38 % yield using preparative HPLC (Scheme 1).

As expected, the presence of atropisomers was detected in these new dendritic systems, in a similar manner to bis-3,4-benzopyrene, for which two atropisomers are possible.[17] The MALDI-TOF mass spectrum of first-generation dendrimer **Py(5)** showed only one molecular peak at *m*/*z* 1228, although the ^{1}H NMR spectrum revealed the existence of several compounds without coalescence. Analytical HPLC confirmed the existence of four out of the five possible atropisomers of **Py(5)** (see the Supporting Information). Following the same approach as for **Py(5)**, the model compound **Py(2)** was obtained in 82 % yield from a Suzuki–Miyaura coupling reaction between 1-bromo-7-*tert*-butylpyrene and 7-*tert*-butylpyrene-1-boronic acid pinacol ester. The presence of the *tert*-butyl group rendered it possible to selectively obtain the 1,3-dibromo-7-*tert*-butylpyrene derivative, which was then reacted in a coupling reaction with 7-*tert*-butylpyrene-1-boronic acid pinacol ester to afford model-compound **Py(3)** in 68 % yield. As predicted, HPLC analysis revealed just one single peak for **Py(2)** because only enantiomers are possible. However, for **Py(3)** the presence of two atropisomers was confirmed.[18]

The absorption and fluorescence spectra of the oligopyrenes **Py(*n*)** ($n = 2$, 3, 5, and 17) in toluene at 25 °C are presented in Figure 4. In the absorption spectra, the vibrational structure of 1-methylpyrene (1-MePy) is still visible. From **Py(2)** to **Py(17)**, the broad absorption band red shifted from the structured part of the spectrum increases in relative intensity. This broad band reflects the intramolecular interaction between the pyrene moieties in the **Py(*n*)** compounds, which becomes stronger from **Py(2)** to **Py(17)**. The extinction coefficient per pyrene subunit at the maximum of the absorption spectrum ε^{max}/n (Table 1) becomes smaller with increasing *n*, from 25180 $M^{-1}cm^{-1}$ for **Py(2)** to 18990 $M^{-1}cm^{-1}$ for **Py(17)**. These values should be compared with the ε^{max} of 1-MePy (39730 $M^{-1}cm^{-1}$) and pyrene (45870 $M^{-1}cm^{-1}$), which show that the minor perturbation by the methyl group in 1-MePy leads to a decrease in ε^{max} (Table 1). The fluorescence spectrum of **Py(2)** consists of a single band, with some vibrational structure. The fluorescence band shifts to the red from 23300 cm^{-1} for **Py(2)** to 20660 cm^{-1} for **Py(17)**, with a simultaneous loss of structure (Figure 4). The fluorescence quantum yields Φ_f of **Py(*n*)** are between 0.72 for **Py(2)** and 0.69 for **Py(17)**.

The fluorescence decays of **Py(2)**, **Py(3)**, and **Py(5)** in toluene at 25 °C, measured at the fluorescence maximum, have a decay time τ_1 of 1.76, 1.86, and 1.51 ns, respectively (Figure 5 and Table 1). In the case of **Py(17)**, a triple-exponential decay is found, with $\tau_1 = 1.75$ ns as the major component. Intermolecular excimer formation with the **Py(*n*)** compounds can be excluded, because of their small concentrations ($< 10^{-5}$ mol L^{-1}) and the short monomer-fluorescence lifetime τ_1 of around 2 ns. From Φ_f and τ_1, the radiative rate

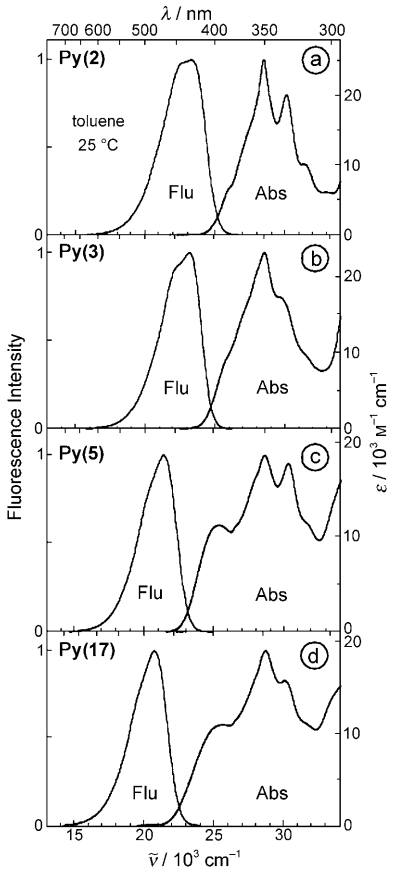


Figure 4. Absorption (Abs) and fluorescence (Flu) spectra of the pyrene oligomers **Py(*n*)** ($n=2$, 3, 5, 17) in toluene at 25 °C. Excitation wavelength $\lambda_{ex}=350$ nm. Solution concentrations: [**Py(2)**] $=0.91\times10^{-5}$ mol L^{-1}; [**Py(3)**] $=0.57\times10^{-5}$ mol L^{-1} [**Py(5)**] $=0.165\times10^{-5}$ mol L^{-1}; [**Py(17)**] $=0.075\times10^{-5}$ mol L^{-1}.

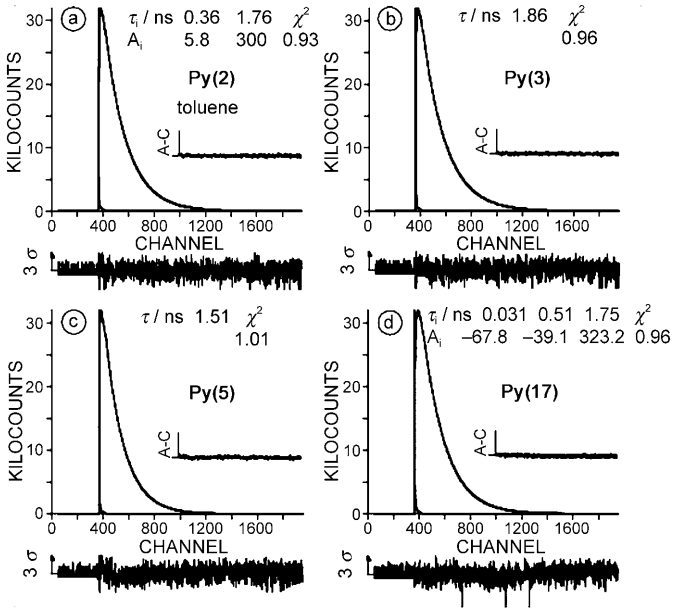


Figure 5. Fluorescence decay of the pyrene oligomers **Py(*n*)** ($n=2$, 3, 5, 17) in toluene at 25 °C. Emission wavelength at the fluorescence maximum (see Figure 4). The weighted deviations σ, the autocorrelation functions A–C and the values for χ^2 are also indicated. $\lambda_{ex}=396$ nm. Time resolution: 10.4 ps/channel with a time window of 1500 effective channels.

constant k_f, a measure of the probability of the $S_1\rightarrow S_0$ transition, was calculated to be between 38.7×10^7 s^{-1} for **Py(3)** and 46.6×10^7 s^{-1} for **Py(5)** (Table 1). These values are more than 100-times larger than those of 1-MePy (0.33×10^7 s^{-1}) and pyrene (0.16×10^7 s^{-1}), indicating that, in the **Py(*n*)** compounds, a state reversal of the $S_1(L_b)$ and $S_2(L_a)$ ordering of 1-MePy and pyrene has taken place.

In summary, we have reported a new type of stiff multichromophoric system, polypyrene dendrimers, incorporating a well-defined number of pyrene units in a confined volume. The rigid and strongly twisted 3D structure allows a precise spatial arrangement in which each unit is a chromophore. The large extinction coefficient and fluorescence quantum yield make these dendrimers attractive candidates for use as fluorescence labels. A detailed study of the excited-state processes in these multichromophoric systems is currently in progress.

Table 1: Data for the Oligopyrenes **Py(2)**, **Py(3)**, **Py(5)**, and **Py(17)** and for 1-methylpyrene (1-MePy) and Pyrene (Py) in Toluene at 25 °C.

Compound	ε_{max}[a] [M^{-1} cm^{-1}] (nm)	ε_{max}/n[b] [M^{-1} cm^{-1}]	Φ(flu)[c]	τ[d] [ns]	k_f[e] [10^7 s^{-1}]	$\tilde{\nu}$(flu)[f] [10^3 cm^{-1}]	$E(S_1)$[g] [10^3 cm^{-1}]
Py(2)	50365 (350.8)	25180	0.72	1.76	40.9	23.30	25.17
Py(3)	69570 (350.6)	23190	0.72	1.86	38.7	23.20	24.70
Py(5)	93730 (349.8)	18750	0.70	1.51	46.6	21.31	23.08
Py(17)	322790 (349.8)	18990	0.69	1.75	39.6	20.66	22.42
1-MePy	39730 (345.6)	39730	0.57[h]	173	0.33	–	26.54
pyrene	45870 (337.8)	45870	0.51[h]	325	0.16	–	26.81

[a] Extinction coefficient at λ_{max} of the absorption spectrum. [b] Extinction coefficient divided by the number of pyrene subunits *n*.[c] Fluorescence quantum yield. [d] Fluorescence decay time. For **Py(17)** the longest decay time is listed (Figure 5 d). With 1-MePy and pyrene the fluorescence lifetime τ_0 (5×10^{-7} M solution, with no excimer formation) is presented. These τ_0 data come from ref. [19]. [e] Radiative rate constant: $k_f=\Phi(\text{flu})/\tau_1$. [f] Maximum of the fluorescence spectrum (Figure 4). [g] Energy of the first excited singlet state S_1, in the case of **Py(*n*)** approximated from the crossing of the absorption and fluorescence spectra. For 1-MePy and pyrene, the energy of the 0–0 vibrational peak in the absorption spectrum is given. [h] For a dilute solution (3×10^{-6} M for 1-MePy, 2×10^{-6} M for Py), with negligible influence of excimer formation, from ref. [20].

Experimental Section

The fluorescence decay times were obtained by time-correlated single

photon counting. The picosecond laser system consists of a mode-locked titanium-sapphire laser (Coherent, MIRA 900F) pumped by an argon ion laser (Coherent, Innova 415).[21] The instrument response function of the laser SPC system has a FWHM of 19 ps. The fluorescence spectra were measured with a quantum-corrected Fluoromax-3 (modified)[21] spectrofluorometer. The absorption spectra were run on a Cary 500 spectrometer.

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[1] a) T. Förster, K. Kasper, *Z. Phys. Chem.* **1954**, *1*, 275 – 277; b) J. B. Birks, D. J. Dyson, I. H. Munro, *Proc. R. Soc. London Ser. A* **1963**, *275*, 575 – 588; c) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, **1970**; d) K. A. Zachariasse, *Trends Photochem. Photobiol.* **1994**, *3*, 211 – 227.

[2] a) K. A. Zachariasse, W. Kühnle, *Z. Phys. Chem. NF* **1976**, *101*, 267 – 276; b) K. A. Zachariasse, G. Duveneck, R. Busse, *J. Am. Chem. Soc.* **1984**, *106*, 1045 – 1051; c) K. A. Zachariasse, R. Busse, G. Duveneck, W. Kühnle, *J. Photochem.* **1985**, *28*, 237 – 253; d) K. A. Zachariasse, G. Duveneck, W. Kühnle, U. Leinhos, P. Reynders in *Photochemical Processes in Organized Molecular Systems* (Ed.: K. Honda), Elsevier, Dordrecht, **1991**, pp. 83 – 100; e) K. A. Zachariasse, A. Maçanita, W. Kühnle, *J. Phys. Chem. B* **1999**, *103*, 9356 – 9365; f) P. Reynders, W. Kühnle, K. A. Zachariasse, *J. Am. Chem. Soc.* **1990**, *112*, 3929 – 3939; g) P. Reynders, W. Kühnle, K. A. Zachariasse, *J. Phys. Chem.* **1990**, *94*, 4073 – 4082; h) K. A. Zachariasse, W. Kühnle, U. Leinhos, P. Reynders, G. Striker, *J. Phys. Chem.* **1991**, *95*, 5476 – 5488.

[3] a) T. Förster; B. K. Selinger, *Z. Naturforsch. A* **1964**, *19*, 38 – 41; b) H. J. Pownall, L. C. Smith, *J. Am. Chem. Soc.* **1973**, *95*, 3136 – 3140; c) K. A. Zachariasse, *Chem. Phys. Lett.* **1978**, *57*, 429 – 432; d) R. Zana, *J. Phys. Chem. B* **1999**, *103*, 9117 – 9125.

[4] a) J. M. Vanderkooi; S. Fischkoff; M. Andrich; F. Podo; C. S. Owen, *J. Chem. Phys.* **1975**, *63*, 3661 – 3666; S. Fischkoff; M. Andrich; F. Podo; C. S. Owen, *J. Chem. Phys.* **1975**, *63*, 3661 – 3666; b) K. A. Zachariasse, W. Kühnle, A. Weller, *Chem. Phys. Lett.* **1980**, *73*, 6 – 11; c) J. Repakova, J. M. Holopainen, M. Karttunen, I. Vattulainen, *J. Phys. Chem. B* **2006**, *110*, 15403 – 15410.

[5] a) R. L. Melnick, H. C. Haspel, M. Goldenberg, L. M. Greenbaum, S. Weinstein, *Biophys. J.*. **1981**, *34*, 499 – 515; b) K. A. Zachariasse, W. L. C. Vaz, C. Sotomayor, W. Kühnle, *Biochim. Biophys. Acta Biomembr.* **1982**, *688*, 323 – 332; c) L. M. Almeida, W. L. C. Vaz, C. K. A. Zachariasse, V. M. C. Madeira, *Biochemistry* **1984**, *88*, 2964 – 2970; d) H. A. Wilson-Ashworth, Q. Bahm, J. Erickson, A. Shinkle, M. P. Vu, D. Woodbury, J. D. Bell, *Biophys. J.* **2006**, *91*, 4091 – 4101.

[6] a) A. Thomas, S. Polarz, M. Antonietti, *J. Phys. Chem. B* **2003**, *107*, 5081 – 5087; b) S. K. Kim, S. H. Lee, J. Y. Lee, J. Y. Lee, R. A. Bartsch, J. S. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 16499 – 16506; c) J. S. Kim, M. G. Choi, K. C. Song, K. T. No, S. Ahn, S.-K. Chang, *Org. Lett.* **2007**, *9*, 1129 – 1132; d) P. Conlon, C. J. Yang, Y. Wu, Y. Chen, K. Martinez, Y. Kim, N. Stevens, A. A. Marti, S. Jockusch, N. J. Turro, W. Tan, *J. Am. Chem. Soc.* **2008**, *130*, 336 – 342.

[7] a) J. K. Thomas, *J. Am. Chem. Soc.* **1977**, *99*, 2039 – 2044; b) D. C. Dong, M. A. Winnik, *Can. J. Chem.* **1984**, *62*, 2560 – 2565.

[8] a) L. Ammerer, A. Zinke, *Monatsh. Chem.* **1953**, *84*, 25 – 31; b) A. J. Fatiadi, *J. Org. Chem.* **1967**, *32*, 2903 – 2904; c) T. von der Haar, A. Hebecker, Yu. V. Il'ichev, Y.-B. Jiang, W. Kühnle, K. A. Zachariasse, *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430 – 442; d) M. Baumgarten, L. Gherghel, J. Friedrich, M. Jurczok, W. Rettig, *J. Phys. Chem. A* **2000**, *104*, 1130 – 1140; e) C.-H. Yang, T.-F. Guo, I.-W. Sun, *J. Lumin.* **2007**, *124*, 93 – 98.

[9] a) J. Bargon, S. Mohmand, R. J. Waltman, *IBM J. Res. Dev.* **1983**, *27*, 330 – 341; b) S. Hino, K. Iwasaki, K. Matsumoto, *Synth. Met.* **1994**, *64*, 259 – 264; c) L. Qu, G. Shi, *Chem. Commun.* **2004**, 2800 – 2801; d) Y. Sakamoto, M. Ichimura, M. Kashiwabara, S. Tamura, US Patent 7,244,516 B1, **2007**.

[10] a) S. Hecht, N. Vladimirov, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2001**, *123*, 18 – 25; b) S. Bernhardt, M. Kastler, V. Enkelmann, M. Baumgarten, K. Müllen, *Chem. Eur. J.* **2006**, *12*, 6117 – 6128.

[11] a) G. M. Stewart, M. A. Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4354 – 4360; b) R. Wilken, J. Adams, *Macromol. Rapid Commun.* **1997**, *18*, 659 – 665; c) R. S. Frank, G. Merkle, M. Gauthier, *Macromolecules* **1997**, *30*, 5397 – 5402; d) L. A. Baker, R. M. Crooks, *Macromolecules* **2000**, *33*, 9034 – 9039; e) C. M. Cardona, T. Wilkes, W. Ong, A. E. Kaifer, T. D. McCarley, S. Pandey, G. A. Baker, M. N. Kane, S. N. Baker, F. V. Bright, *J. Phys. Chem. B* **2002**, *106*, 8649 – 8656; f) L. Brauge, G. Vériot, G. Franc, R. Deloncle, A.-M. Caminade, J.-P. Majoral, *Tetrahedron* **2006**, *62*, 11891 – 11899.

[12] C. Modrakowski, S. C. Flores, M. Beinhoff, A. D. Schlüter, *Synthesis* **2001**, 2143 – 2155.

[13] a) F. Morgenroth, K. Müllen, *Tetrahedron* **1997**, *53*, 15349 – 15366; b) F. Morgenroth, A. J. Berresheim, M. Wagner, K. Müllen, *Chem. Commun.* **1998**, 1139 – 1140; c) F. Morgenroth, C. Kubel, M. Muller, U. M. Wiesler, A. J. Berresheim, M. Wagner, K. Müllen, *Carbon* **1998**, *36*, 833 – 837.

[14] a) F. Morgenroth, C. Kübel, K. Müllen, *J. Mater. Chem.* **1997**, *7*, 1207; b) J. Hofkens, M. Maus, T. Gensch, T. Vosch, M. Cotlet, F. Köhn, A. Herrmann, K. Müllen, F. De Schryver, *J. Am. Chem. Soc.* **2000**, *122*, 9278 – 9288; c) A. C. Grimsdale, T. Vosch, M. Lor, M. Cotlet, S. Habuchi, J. Hofkens, F. De Schryver, K. Müllen, *J. Lumin.* **2005**, *111*, 239 – 253; d) C. Flors, I. Oesterling, T. Schnitzler, E. Fron, G. Schweitzer, M. Sliwa, A. Herrmann, M. van der Auweraer, F. De Schryver, K. Müllen, J. Hofkens, *J. Phys. Chem. C* **2007**, *111*, 4861 – 4870.

[15] Y. Miura, E. Yamano, A. Tanaka, J. Yamauchi, *J. Org. Chem.* **1994**, *59*, 3294 – 3300.

[16] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457 – 2483.

[17] M. Wilk, W. Bez, J. Rochlitz, *Tetrahedron* **1966**, *22*, 2599 – 2608.

[18] The different atropisomer ratios and interconversion will be the topic of a separate paper based on kinetic studies.

[19] a) P. Reynders, PhD Thesis, University Göttingen, **1988**; b) K. A. Zachariasse, unpublished results.

[20] A. Demeter, K. A. Zachariasse, in preparation.

[21] S. I. Druzhinin, N. P. Ernsting, S. A. Kovalenko, L. P. Lustres. T. A. Senyushkina, K. A. Zachariasse, *J. Phys. Chem. A* **2006**, *110*, 2955 – 2969.

