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## Polyphenylene Dendrimers with Different Fluorescent Chromophores Asymmetrically Distributed at the Periphery

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## Experimental

**General Information** The solvents were used of commercial p. a. quality; tetrahydrofuran (THF) was dried over potassium, toluene was distilled from sodium. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker DRX 500 (500 MHz and 125 MHz respectively) or Bruker AMX 300 (300 MHz and 75 MHz respectively). Mass spectra were recorded on a Bruker MALDI-TOF. UV-Vis data were obtained on a Perkin-Elmer Lambda 9 and fluorescence spectra were measured on a SPEX Fluorolog 2 Type 212 spectrometer. Tetrakis(triphenylphosphine)-palladium (0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) and dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloromethane adduct (Pd(dppf)) catalysts were purchased from ABCR.

**2:** Tetra-(4-ethynylphen-1-yl)-methan (**1**) (2 g, 4.8 mmol) was dissolved in 60 ml THF and n-BuLi (6 ml, 9.6 mmol, 1.6 M) was added slowly at -70°C. After stirring for 2h at -78°C, TipsCl (4.17 ml, 19.2 mmol) was added and the solution was allowed to warm up to RT over 3 h. The reaction mixture was extracted with H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>, and the organic phase was dried with MgSO<sub>4</sub>. The product mixture was purified by column chromatography (PE/CH<sub>2</sub>Cl<sub>2</sub> 10:1) to afford **2** (1 g, yield: 36 %) as a white solid. R<sub>f</sub> = 0.21, mp > 300°C, <sup>1</sup>H-NMR (300 MHz, THF d<sub>8</sub>, 353 K) δ 7.37 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 9.21 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 3.52 (s, 3 H); 1.15-1.13 (m, 21 H); <sup>13</sup>C-NMR (75.5 MHz, THF d<sub>8</sub>, 303K) δ 12.25, 19.03, 65.88 (q), 79.09, 83.81 (q), 91.02 (-C≡C-TiPS), 108.14 (-C≡C-TiPS), 121.66 (q), 122.37 (q), 131.6 CH<sub>arom</sub> 132.33 (CH<sub>arom</sub>), 147.29 (q); MS (FD, 8kV) m/z (%) 572 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>42</sub>H<sub>40</sub>Si: C, 88.06; H, 7.04; Found: C, 88.04; H, 6.98.

**3:** Tetra-(4-ethynylphen-1-yl)-methan (**1**) (2 g, 4.8 mmol), 60 ml THF and n-BuLi (6 ml, 9.6 mmol, 1.6 M) were used by the same method as described above. The product mixture was purified by column chromatography (PE/CH<sub>2</sub>Cl<sub>2</sub> 10:1, R<sub>f</sub> = 0.37), to afford **3** as a white solid (1.6 g, yield: 47 %) mp > 300°C, <sup>1</sup>H-NMR (300 MHz, THF d<sub>8</sub>, 353 K) δ 7.37 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 9.21 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 3.52 (s, 2 H); 1.15-1.13 (m, 42 H); <sup>13</sup>C-NMR (75.5 MHz, THF d<sub>8</sub>, 303K) δ 12.25 (-CH-CH<sub>3</sub>), 19.03 (-CH-CH<sub>3</sub>), 65.88 (q), 79.09 (-C≡CH), 83.81 (-C≡CH), 91.02 (-C≡C-TiPS), 108.14 (-C≡C-TiPS), 121.66 (q), 122.37 (q), 131.6 CH<sub>arom</sub> 132.33 (CH<sub>arom</sub>), 147.29 (q); MS (FD, 8kV) m/z (%) 728 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>51</sub>H<sub>60</sub>Si<sub>2</sub>: C, 84.00; H, 8.29; Found: C, 83.91; H, 8.38.

**4:** Tetra-(4-ethynylphen-1-yl)-methan (**1**) (2 g, 4.8 mmol), 60 ml THF and n-BuLi (6 ml, 9.6 mmol, 1.6 M) were used by the same method as described above. The product mixture was purified by column chromatography (PE/CH<sub>2</sub>Cl<sub>2</sub> 20:1, R<sub>f</sub> = 0.62), to afford **4** (250 mg, yield: 6 %) as a white solid, mp > 300°C, <sup>1</sup>H-NMR (300 MHz, THF d<sub>8</sub>, 353 K) δ 7.37 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 9.21 (d, <sup>3</sup>J = 8.4 Hz, 8 H); 3.52 (s, 1 H); 1.15-1.13 (m, 63 H); <sup>13</sup>C-NMR (75.5 MHz, THF d<sub>8</sub>, 303K) δ 12.13 (-CH-CH<sub>3</sub>), 18.9 (-CH-CH<sub>3</sub>), 65.70 (q), 78.99 (-C≡CH), 83.68 (-C≡CH), 90.91 (-C≡C-TiPS), 108.00 (-C≡C-TiPS), 121.57 (q), 122.27 (q), 131.55 CH<sub>arom</sub> 132.19 (CH<sub>arom</sub>), 147.14 (q); MS (FD, 8kV) m/z (%) 884 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>60</sub>H<sub>80</sub>Si<sub>3</sub>: C, 81.38; H, 9.11 Found: C, 81.30; H, 9.16

N-(2,6-Diisopropylphenyl)-14-brom-1,6-di(4-t-butylphenoxy)-11(CO),12-benzoylterrylen - 3,4-dicarboximid (**8**):

Bromine (1.28 g, 7.98 mmol) was added to a stirred solution of **7** (1.99 mmol) in 100 ml CHCl<sub>3</sub> at RT. After 16 h, twofold bromination became evident (tlc monitoring), and the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (CHCl<sub>3</sub>) to afford **8** (1.71 g, 79%) as a blue solid: mp > 300°C, <sup>1</sup>H-NMR (500 MHz, C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>, 353 K) δ 9.28 (d, <sup>3</sup>J = 9.2 Hz, 1 H); 9.21 (d, <sup>3</sup>J = 9.2 Hz, 1 H); 9.08 (d, <sup>3</sup>J = 8.0 Hz, 1 H); 8.38 (s, 1 H); 8.31 (d, <sup>3</sup>J = 8.6 Hz, 1 H); 8.18 (s, 1 H); 8.08 (s, 1 H); 8.02 (m, 3

H); 7.87 (d,  $^3J = 8$  Hz, 1 H); 7.53 (d,  $^3J = 8.6$  Hz, 2 H); 7.47 (d,  $^3J = 8.6$  Hz, 2 H); 7.38 (m, 2 H); 7.28 (d,  $^3J = 8.6$  Hz, 2 H); 7.27 (d,  $^3J = 7.4$  Hz, 2 H); 7.23 (t,  $^3J = 9.2$ , 1 H); 7.14 (d,  $^3J = 8.6$  Hz, 2 H); 2.77 (sept.,  $^3J = 6.8$  Hz, 2 H); 1.40 (s, 9 H), 1.37 (s, 9 H); 1.18 (d,  $^3J = 6.7$  Hz, 12 H)  $^{13}\text{C-NMR}$  (125.5 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 353K)  $\delta$  186.32 (C=O); 166.88 (C=O); 156.23; 156.03; 154.21; 154.01; 150.91; 150.56; 148.06; 145.07; 141.33; 141.09; 139.79; 139.37; 137.91; 136.99; 134.48; 133.78; 133.51; 133.39; 133.20; 133.04; 132.88; 132.71; 132.44; 132.14; 132.00; 131.92; 131.67; 131.37; 131.23; 131.03; 130.90; 130.63; 130.44; 130.19; 130.05; 129.78; 129.09; 128.86; 128.33; 128.21; 128.03; 127.47; 127.13; 126.56; 125.39; 124.59; 124.73; 124.02; 121.41; 121.18; 120.39; 119.77; 35.98; 33.67; 31.57; 25.02; MS (FD, 8kV)  $m/z$  (%) 1082.9 (100 %) [ $\text{M}^+$ ]. Anal. Calcd. for  $\text{C}_{71}\text{H}_{56}\text{BrNO}_5$ : C, 78.73; H, 5.21; N, 1.29; Found: C, 78.46; H, 5.21; N, 1.26

**12:** A mixture of **9** (1.5 g, 3.24 mmol), **10** (2.47 g, 9.71 mmol) and potassium acetate (953 mg, 9.71 mmol) was dissolved in 80 ml DMSO under an argon atmosphere. Pd-dppf catalyst (119 mg 0.162 mmol) was added and the resulting mixture was stirred 12 h at 75°C, and thereafter washed with water and  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$  layer was separated and dried over  $\text{MgSO}_4$ . A field desorption mass-spectrum (8 kV) of the crude product **11** showed only the product peak. Without further work-up **11** (66 mg, 0.13 mmol) and **8** (70 mg, 0.065 mmol) were dissolved in 3 ml toluene, 0.5 ml EtOH and 1.5 ml of a solution of 0.41 g  $\text{K}_2\text{CO}_3$  in  $\text{H}_2\text{O}$  (2 M) was added and the reaction mixture was flushed with argon.  $\text{Pd}(\text{PPh}_3)_4$  catalyst (4 mg, 0.003 mmol) was added and the reaction mixture was stirred at 80°C for 12 h. The resulting solution was washed three times with  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$ . The organic layer was separated and dried over  $\text{MgSO}_4$ . The crude product was purified by chromatography eluting with  $\text{CH}_2\text{Cl}_2$  to give **12** as a dark blue powder (79 mg, 87 %), mp: 183°C,  $^1\text{H-NMR}$  (500 MHz,  $\text{C}_2\text{Cl}_4\text{D}_2$ , 353 K)  $\delta$  9.09 (d,  $^3J = 8.76$  Hz, 1 H); 9.08 (d,  $^3J = 8.0$  Hz, 1 H); 8.96 (d,  $^3J = 8.76$  Hz, 1 H); 8.38 (s, 1 H); 8.22 (s, 1 H); 8.00 (m, 3 H); 7.88 (m, 2 H); 7.77 (d,  $^3J = 8$  Hz, 1 H); 7.51 - 7.01 (m, 29 H); 6.87 (d,  $^3J = 6.5$  Hz, 2 H); 6.71 (d,  $^3J = 8.2$  Hz, 2 H); 2.77 (sept.,  $^3J = 6.8$  Hz, 2 H); 1.45 (s, 9 H), 1.27 (s, 9 H); 1.16 (d,  $^3J = 6.7$  Hz, 12 H)  $^{13}\text{C-NMR}$  (125.5 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 353K)  $\delta$  186.32 (C=O); 166.88 (C=O); 164.23 (C=O); 156.23; 156.03; 154.73; 154.21; 154.00; 150.88; 150.53; 147.86; 145.87; 141.37; 141.29; 139.76; 139.35; 137.88; 136.99; 134.51; 133.83; 133.54; 133.41; 133.21; 132.98; 132.89; 132.79; 132.51; 132.23; 131.99; 131.96; 131.63; 131.32; 131.27; 131.11; 130.97; 130.60; 130.19; 130.04; 129.82; 129.32; 128.86; 128.34; 128.21; 127.98; 127.76; 127.19; 126.10; 125.61; 124.87; 124.49; 124.02; 121.41; 121.18; 120.70; 120.52; 19.69; 119.31; 35.98; 31.65; 30.11; 24.03; MS (FD, 8kV)  $m/z$  (%) 1386 (100%,  $\text{M}^+$ ), 693 (12%,  $\text{M}^{2+}$ ). Anal. Calcd. for  $\text{C}_{100}\text{H}_{75}\text{NO}_6$ : C, 86.62; H, 5.45, N, 1.01 Found: C, 86.49 H, 5.34 N, 1.00

### 13: 4,4'-Diethynylbenzil (13)

4,4'-Bis-(tri-*iso*-propylsilylethynyl)-benzil (20.0 g, 35.0 mmol) and KF (6.1 g, 105.1 mmol) were dissolved in 400 ml DMF and 20 ml acetic acid and stirred for 12 h at RT. The reaction mixture was extracted with  $\text{NaHCO}_3$  /  $\text{CH}_2\text{Cl}_2$ , and the organic phase was dried with  $\text{MgSO}_4$ . After evaporation of the solvent under reduced pressure the crude product was dissolved in diethylether. The product crystallized at -18 °C (yield: 6.6 g 0.026 mmol; 73 %) as light yellow crystals, mp: >300 °C;  $^1\text{H-NMR}$ : (300MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 303K):  $\delta$  7.85 (d,  $^3J = 8.4$  Hz, 4 H); 7.64 (d,  $^3J = 8.4$  Hz, 4 H); 3.33 (s, 2 H);  $^{13}\text{C-NMR}$  (75 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 303 K):  $\delta$  193.4; 133.0; 132.6; 130.0; 129.9; 82.9; 82.5; MS (FD, 8kV)  $m/z$  (%)  $m/z$  [ $\text{ue}^{-1}$ ]: 258,2 (100 %,  $\text{M}^+$ ). Anal. Calcd. for  $\text{C}_{18}\text{H}_{10}\text{O}_2$ : C 83.71 %, H 3.90 % Found: C 83.62 %, H 4.00 %

**15:** **13** (0.5 g, 1.94 mmol) and **14** (2.24 g, 5.82 mmol) in 25 ml *o*-xylene were heated overnight at 170°C under an argon atmosphere. The reaction mixture was precipitated from pentane until the dark red color of **14** had disappeared. **15** was obtained as a bright yellow

amorphous powder (1.9 g, 98 %), mp: > 300°C, <sup>1</sup>H-NMR: (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 303 K): δ 7.67 (d, <sup>3</sup>J = 8.4 Hz, 4 H); 7.47 (s, 2 H); 7.25 (d, <sup>3</sup>J = 8.4 Hz, 4 H); 7.09 (m, 10 H); 6.90-6.67 (m, 30 H); <sup>13</sup>C-NMR: (75 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>/CS<sub>2</sub>, 303 K): δ 196.1; 150.8, 143.8, 143.2, 142.6, 142.0, 141.6, 141.4, 141.1, 140.9, 140.7, 133.2, 132.8, 132.4, 131.7, 131.1, 129.4, 128.9, 128.7, 128.4, 128.1, 127.7, 127.4, 127.1, 150.8, 143.8, 143.2, 142.6, 142.0, 141.6, 141.4, 141.1, 140.9, 140.7 (q); 133.2, 132.8, 132.4, 131.7, 131.1, 129.4, 128.9, 128.7, 128.4, 128.1, 127.7, 127.4, 127.1 (t); MS (FD, 8kV) m/z (%) m/z [ue<sup>-1</sup>]: 970,8 (100 %, M<sup>+</sup>); 485.4 (23 %, M<sup>2+</sup>). Anal. Calcd. for C<sub>74</sub>H<sub>50</sub>O<sub>2</sub>: C 91,52 %, H 5,19 % Found: C 92,66 %, H 5,14 %

**17:** 1,3-diphenylacetone (**16**) (238 mg, 1.13 mmol) and (1.0 g, 1.03 mmol) **15** were dissolved in 2 ml 1,4-dioxan. The reaction mixture was heated to 80 °C and 2.6 ml (2.06 mmol) Bu<sub>4</sub>NOH in MeOH (0.8 M) was added, where upon the solution immediately turned brown. The solvent was evaporated after 1 h and the product precipitated from EtOH to give **17** as a light brown powder (1.10 g, 93 %), mp: >300 °C; <sup>1</sup>H-NMR (300MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 383 K): δ 7.45 (s, 2 H); 7.25 (d, <sup>3</sup>J = 8.4 Hz, 4H); 7.22-7.16 (m, 4 H); 7.12-7.06 (m, 10 H); 6.90-6.67 (m, 30 H); 7.25 (d, <sup>3</sup>J = 8.4 Hz, 4 H); <sup>13</sup>C-NMR: (75 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>/CS<sub>2</sub>, 303 K): δ 200.4; 154.4, 142.5, 142.00, 141.9, 141.0, 140.4, 140.3, 140.00, 139.9, 139.4 (q); 131.7, 131.6, 131.2 (q); 131.0, 130.7 (q); 130.4, 130.2, 129.7, 129.2, 128.3, 127.9, 127.7, 127.2, 127.1, 126.9, 126.6, 126.1, 125.8, 125.6, 125.4, 154.4, 142.5, 141.9, 141.9, 141.0, 140.3, 140.3, 140.00, 139.9, 139.4, 131.7, 131.6, 131.2, 131.0, 130.7, 130.4, 130.2, 129.7, 129.2, 128.3, 127.9, 127.7, 127.2, 127.1, 126.9, 126.6, 126.1, 125.8, 125.6 (q); 125.4 (q); MS (FD, 8kV) m/z (%) m/z [ue<sup>-1</sup>]: 1145.0 (100 %, M<sup>+</sup>). Anal. Calcd. for C<sub>89</sub>H<sub>60</sub>O: C 93.32 %, H 5.28 % Found: C 93.41 %, H 5.36 %.

**18:** **13** (3 g, 11.6 mmol) and **14** (4.19 g, 12.7 mmol) in 100 ml o-xylene were heated 12 h at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2) to give **18** as dark orange crystals (2.59 g, 36 %), mp: <300°C, <sup>1</sup>H-NMR (300 MHz, THF d<sub>8</sub>, 303 K): δ 7.90 (d, <sup>3</sup>J = 8.7 Hz, 2 H); 7.76 (d, <sup>3</sup>J = 8.4 Hz, 2 H); 7.62 (d, <sup>3</sup>J = 8.8 Hz, 2 H); 7.53 (s, 1 H); 7.34 (d, <sup>3</sup>J = 8.4 Hz, 2 H); 7.17 (s, 4 H); 7.00-6.81 (m, 16 H); 3.39 (s, 1 H); <sup>13</sup>C-NMR (75.5 MHz, THF d<sub>8</sub>, 303K): δ 149.78; 142.90; 142.29; 141.86; 141.15; 140.87; 140.66; 140.31; 140.06; 140.03; 133.49; 133.34; 132.22; 132.17; 131.66; 131.41; 130.63; 130.43; 130.22; 129.95; 129.39; 128.38; 127.88; 127.64; 127.39; 127.17; 126.79; 126.50; 126.23; 83.13; 82.18; MS (FD, 8kV) m/z (%) 614 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>46</sub>H<sub>30</sub>O<sub>2</sub>: C, 89.88; H, 4.92 Found: C, 89.95; H, 4.57

**19:** **18** (2.19 g, 3.55 mmol) and **9** (1.97 g, 4.27 mmol) in 50 ml o-xylene were heated 12 h at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:3) to give **19** as a yellow powder (3.35 g, 90 %), mp: >300°C, <sup>1</sup>H-NMR (300 MHz, THF d<sub>8</sub>, 303 K): δ 7.73 (d, <sup>3</sup>J = 8.31; 4 H); 7.53 (d, <sup>3</sup>J = 3.8, 2 H); 7.33-7.29 (m = 4 H); 7.17 (s, 8 H); 7.08 (d, <sup>3</sup>J = 8.76, 2 H); 7.05-6.80 (m, 25H); 6.78-6.69 (m, 4H); <sup>13</sup>C-NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 303 K): δ 194.24; 142.54; 142.44; 141.94; 141.74; 141.63; 141.60; 141.50; 141.43; 141.21; 140.76; 140.54; 140.30; 140.21; 140.08; 139.96; 139.86; 139.78; 139.63; 139.46; 139.41; 131.81; 131.33; 130.48; 130.26; 129.55; 128.22; 128.02; 127.75; 127.51; 127.25; 127.03; 126.91; 126.82; 126.69; 126.42; 126.14; 125.88; 120.30; 120.02; MS (FD, 8kV) m/z (%) 1050 (100 %, M<sup>+</sup>), 525 (15 %, M<sup>2+</sup>) 15 %. Anal. Calcd. for C<sub>74</sub>H<sub>49</sub>BrO<sub>2</sub>: C, 84.64; H, 70 Found: C, 84.51; H, 4.68

**20:** **19** (3 g, 2.8 mmol) and **16** (0.631 g, 2.99 mmol) in 90 ml toluene were heated at 90°C. 1.9 ml Bu<sub>4</sub>NOH in MeOH (0.8 M) was added and the reaction mixture was stirred for 45 min at

90°C. The resulting solution was washed three times with H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and dried over MgSO<sub>4</sub>. The crude product was purified by chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:1) to give **20** as a brown powder (2.1 g, 61 %); mp: < 300 °C, <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 383K): δ 7.52 (m, 2 H); 7.28-7.13 (m, 20 H); 7.07 (d, <sup>3</sup>J = 8.4 Hz, 2 H); 7.01-6.81 (m, 305 H); 6.77 (d, <sup>3</sup>J = 8.4 Hz, 2 H); 6.65 (d, <sup>3</sup>J = 8.0, 4 H); <sup>13</sup>CNMR: (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 303 K): δ 200.41; 154.52, 142.64, 142.48, 142.20, 142.09; 141.86, 141.24; 141.06; 140.82, 140.70, 140.49, 140.36; 140.17; 140.10; 139.86, 139.71; 139.67; 138.75; 131.7, 131.6, 131.2 (q); 131.0, 130.7 (q); 130.4, 130.2, 129.7, 129.2, 128.3, 127.9, 127.7, 127.2, 127.1, 126.9, 126.6, 126.1, 125.8, 125.6, 125.4, 154.4, 142.5, 141.9, 141.9, 141.0, 140.3, 140.3, 140.00, 139.9, 139.4, 133.63, 131.90, 131.46, 131.30, 131.21, 130.55, 130.32, 129.81, 129.27, 128.38, 128.18, 127.98, 127.73, 127.45, 127.23, 126.97, 126.27, 126.3, 126.04; 125.78 (q); MS (FD, 8kV) m/z (%) 1224 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>89</sub>H<sub>59</sub>BrO: C, 87.31; H, 4.86 Found: C, 86.98; H, 4.87

**22**: A mixture of **20** (3.5 g, 8.92 mmol), **10** (3.4 g, 13 mmol) and potassium acetate (2.9 g, 30 mmol) were dissolved in 150 ml dioxane under an argon atmosphere. Pd-dppf-catalyst (0.326 g, 0.446 mmol) was added and the resulting solution was stirred 12 h at 75°C. The crude mixture was washed with water and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and dried over MgSO<sub>4</sub>. A field desorption mass-spectrum of the crude product **1** showed only the product peak. Without further work-up, **11** (1 g, 0.816 mmol) and **6** (0.450 g, 1.4 mmol) were dissolved in 30 ml toluene. 2 ml EtOH, 10 ml of a solution of 3.2 g K<sub>2</sub>CO<sub>3</sub> in deionized H<sub>2</sub>O (2.3 M) were added, and the mixture was flushed with argon. Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyst (50 mg, 0.043 mmol) was added and the reaction mixture was stirred at 80°C 12 h. The resulting solution was washed three times with H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and dried over MgSO<sub>4</sub>. The crude product was purified by chromatography first eluting with CH<sub>2</sub>Cl<sub>2</sub> (R<sub>f</sub>: 0.77). Mixed fractions were purified via column chromatography again by using CH<sub>2</sub>Cl<sub>2</sub>/PE (1.5:1, R<sub>f</sub>: 0.2) to give **22** as a dark red powder (0.5 g, 38 %), mp: <300°C, <sup>1</sup>H-NMR (300 MHz, THF, 383 K): δ 7.55 (m, 6 H); 7.86–6.68 (m, 65 H); 2.80 (sept., 2H); 1.17 (d, <sup>3</sup>J = 6.95, 12 H); <sup>13</sup>CNMR: (75 MHz, THF, 303 K): δ 199.88; 164.30; 154.62; 146.81; 144.00; 143.27; 143.17; 142.93; 142.76; 141.97; 141.62; 141.42; 141.29; 141.06; 140.98; 140.86 140.67 140.41 140.31 138.38 138.22 138.15 133.58 132.51 132.02 131.87 131.72; 131.37; 131.06; 130.94; 130.74; 130.40; 130.24; 129.95; 129.58; 129.47; 128.63; 128.38; 127.98; 127.70; 127.43; 127.06; 126.71; 126.40; 126.15; 126.00; 124.94; 124.56; 124.29; 122.16; 122.04; 121.42; 121.18; 29.98; 24.31; MS (FD, 8kV) m/z (%): 1625 (100 %, M<sup>+</sup>); 812 (22 %, M<sup>2+</sup>). Anal. Calcd. for C<sub>123</sub>H<sub>85</sub>NO<sub>3</sub>: C, 90.91; H, 5.27; N, 0.86; Found: C, 90.89; H, 5.52 N, 0.79

The synthetic procedure for **23b/c** is similar to that of **23a**, the procedure for the synthesis of **24a** corresponds to that of **24b/c** and **25c-e** corresponds to **25a**.

**23a**: **4** (0.2 g, 0.22 mmol) and **6** (0.244 g, 0.28 mmol) in 3 ml o-xylene were heated 12 h at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> to give **23a** as red powder (0.352 g, 93 %), mp: > 300°C; <sup>1</sup>H-NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 293 K): δ 8.38 (m, 2 H); 8.0 (m, 4 H); 7.6-6.91 (m, 42 H); 2.79 (sept., <sup>3</sup>J = 6.60 Hz, 2 H); 1.18-1.01 (d, <sup>3</sup>J = 6.8 Hz, 75 H), <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 164.23 (C=O); 146.55; 144.21; 141.98; 141.83; 140.91; 140.56; 140.50; 140.02; 139.83; 139.13; 138.91; 137.88; 137.52; 132.01; 131.68; 131.45; 130.79; 130.34; 129.03; 128.19; 127.56; 127.18; 126.63; 123.87; 121.11; 120.53; 120.89; 119.32; 84.86; 77.32; 29.45; 24.26; 17.89, 11.36; (CHCl<sub>3</sub>); MS (FD, 8kV) m/z (%) 1721 (100 %) [M<sup>+</sup>]; 860 (31 %) [M<sup>2+</sup>]. Anal. Calcd. for C<sub>122</sub>H<sub>125</sub>NO<sub>2</sub>Si<sub>3</sub>: C, 85.12; H, 7.32, N, 0.81; Found: C, 85.03; H, 7.17, N, 0.91

**23b:** **3** (0.08 g, 0.11 mmol) and **6** (0.371 g, 0.13 mmol) were reacted in 2 ml o-xylene by above procedure. Column chromatography CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2, R<sub>f</sub> 0.62) gave **23b** (0.306 g, 93%), mp > 300 °C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 383K): δ; 8.63-8.60 (m, broad, 4 H); 8.50-8.41 (m, 8 H); 7.61-7.59 (m, 2 H); 7.52-6.8 (m, 66 H); 2.75 (sept., <sup>3</sup>J = 6.60 Hz, 4H); 1.2-1.05 (m, 66 H); <sup>13</sup>C-NMR: (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 303 K): δ <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 164.33 (C=O); 147.53; 146.46; 144.15; 141.97; 141.65; 141.32; 140.93; 140.65; 140.40; 140.16; 139.83; 139.15; 138.94; 137.83; 137.60; 132.11; 131.65; 131.45; 130.60; 130.39; 129.57; 128.32; 128.04; 127.51; 127.27; 126.96; 124.58; 124.09; 123.71; 121.13; 120.84; 120.33; 120.21; 83.98; 77.19; 29.57; 24.26; 18.14; 11.77; MS (FD, 8kV) m/z (%) 2401 (100 %) [M<sup>+</sup>]; 1200 (47 %) [M<sup>2+</sup>]; 600 (7 %) [M<sup>3+</sup>]; Anal. Calcd. for C<sub>175</sub>H<sub>150</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: C, 87.53; H, 6.30; N, 1.17; Found: C, 87.30; H, 6.16; N, 1.02;

**23c:** **2** (0.088 g, 0.10 mmol) and **6** (0.171 g, 0.085 mmol) were reacted in 2 ml o-xylene by above procedure. Column chromatography CH<sub>2</sub>Cl<sub>2</sub>/PE (1:4, R<sub>f</sub> 0.46) gave **23c** (0.190 g, 95%); m.p > 300°C; <sup>1</sup>H-NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 293 K): δ 8.53 (m, 6 H); 8.37-8.33 (m, 12 H); 7.67 (d, <sup>3</sup>J = 7.69; 2 H); 7.67-6.89 (m, broad, 85 H); 6.9-6.8 (m, 6 H); 2.76 (sept., <sup>3</sup>J = 6.60 Hz, 6 H); 1.16-1.05 (m, <sup>3</sup>J = 6.43 Hz, 57 H), <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 164.41 (C=O); 147.55; 146.54; 144.71; 143.73; 142.15; 141.48; 140.67; 140.53; 140.03; 139.77; 139.21; 138.09; 137.87; 137.51; 132.98; 131.44; 130.94; 130.61; 130.57; 130.44; 129.87; 128.81; 128.66; 128.18; 128.03; 127.79; 126.82; 124.42; 123.93; 121.60; 120.34; 120.22; 120.00; 82.97; 77.08; 29.53; 24.15; 18.96; 11.63; MS (FD, 8kV) m/z (%) 3081 (100 %) [M<sup>+</sup>]; 1540 (23 %) [M<sup>2+</sup>]; 1027 (14 %) [M<sup>3+</sup>]; Anal. Calcd. for C<sub>228</sub>H<sub>175</sub>N<sub>3</sub>O<sub>6</sub>Si: C, 88.88; H, 5.73; N, 1.36; Found: C, 89.40; H, 5.52; N, 1.31;

The synthetic procedure for **24b/c** is similar to that of **24a**, the procedure for the synthesis of **25b-e** corresponds to that of **25a**.

**24a:** **23a** (0.2 g, 0.16 mmol) and NH<sub>4</sub>F (0.035 mg, 0.96 mmol) were dissolved in 10 ml THF under an argon atmosphere. Catalytic amounts of Bu<sub>4</sub>NF dissolved in 1 ml THF were added and the reaction mixture was stirred for a further 2 h. The solution was washed three times with H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>. The organic solvent was evaporated and the crude product was reprecipitated from a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> into 70 ml MeOH to give **24a** as a red powder (110 mg, 96 %), mp: <300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 8.38 (m, 2 H); 8.0 (m, 4 H); 7.6-6.91 (m, 42 H); 3.68 (s, 3 H); 2.79 (sept., <sup>3</sup>J = 6.60 Hz, 2 H); 1.18 (d, <sup>3</sup>J = 6.8 Hz, 12 H), <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 164.27 (C=O); 146.58; 144.18; 142.01; 141.63; 140.90; 140.60; 140.49; 140.11; 139.81; 139.135; 138.84; 137.80; 137.67; 132.14; 131.63; 131.47; 130.72; 130.44; 129.06; 128.19; 127.55; 127.13; 126.95; 123.84; 121.13; 120.86; 120.33; 120.04; 84.87; 77.01; 29.45; 24.26; (CHCl<sub>3</sub>): MS (FD, 8kV) m/z (%): 1252 (100 %) [M<sup>+</sup>]; Anal. Calcd. for C<sub>59</sub>H<sub>65</sub>NO<sub>2</sub>: C, 91.10; H, 5.23, N, 1.12; Found: C, 91.34; H, 5.37, N, 0.92;

**24b:** **23b** (0.25 g, 0.08 mmol) and NH<sub>4</sub>F (0.0125 g, 0.337 mmol) were reacted in 9 ml THF as described above. (0.197 g, 92 %) of **24b** was obtained as a red solid, mp: > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 8.42 (m, 4 H); 8.11-8.10 (m, 8 H); 7.67 (m, 2 H); 7.6-6.85 (m, broad, 66 H); 3.70 (s, 2 H); 2.82 (sept., <sup>3</sup>J = 6.60 Hz, 4 H); 1.21 (d, <sup>3</sup>J = 6.87 Hz, 24 H), <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 164.33 (C=O); 147.57; 146.49; 144.18; 142.01; 141.63; 141.32; 140.90; 140.60; 140.44; 140.16; 139.81; 139.133; 138.88; 137.80; 137.60; 132.08; 131.61; 131.44; 130.57; 130.38; 129.59; 128.32; 128.05; 127.51; 127.25; 126.92; 124.41; 124.09; 123.69; 121.08; 120.97; 120.30; 120.04; 83.67; 77.75; 29.58; 24.35; (CHCl<sub>3</sub>): MS

(FD, 8kV) m/z (%): 2322 (100 %) [ $M^+$ ]; Anal. Calcd. for  $C_{157}H_{110}N_2O_4$ : C, 90.29; H, 5.31; N, 1.34; Found: C, 90.71; H, 5.16; N, 1.29;

**24c:** **23c** (0.150 g, 0.047 mmol) and  $NH_4F$  (3.57 mg, 0.94 mmol) were reacted in 7 ml THF as described above. (0.104 g, 76 %) of **24c** was obtained as a red solid; mp: > 300°C;  $^1H$ -NMR (300 MHz,  $C_2D_2Cl_4$ , 293 K):  $\delta$  8.53 (m, 6 H); 8.33-8.30 (m, 12 H); 7.67 (d,  $^3J = 7.69$ ; 2 H); 7.65-6.91 (m, broad, 85 H); 6.9-6.8 (m, 6 H); 3.16 (s, 2 H); 2.78 (sept,  $^3J = 6.60$  Hz, 6 H); 1.17 (d,  $^3J = 6.48$  Hz, 36 H),  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  164.42 (C=O); 147.57; 146.55; 144.65; 143.71; 142.19; 141.20; 140.99; 140.64; 140.11; 139.77; 139.02; 138.04; 137.87; 137.53; 133.05; 131.45; 130.90; 130.73; 130.57; 130.43; 129.44; 128.99; 128.54; 128.17; 128.08; 127.28; 126.91; 124.40; 123.89; 121.24; 120.62; 120.29; 120.01; 82.94; 77.08; 29.53; 24.15; ( $CHCl_3$ ): MS (FD, 8kV) m/z (%): 2322 (100 %) [ $M^+$ ]; Anal. Calcd. for  $C_{219}H_{155}N_3O_6$ : C, 89.94; H, 5.34; N, 1.44; Found: C, 90.35; H, 5.21; N, 1.40;

**25a:** **24a** (0.1 g, 0.08 mmol) and **14** (0.115 g, 0.3 mmol) in 2 ml o-xylene were heated 12 h at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography with  $CH_2Cl_2$  until all unreacted **14** was eluted. **25a** was washed from the column with THF to give **25a** as a red powder (0.176 g, 95 %); mp: >300°C, UV/VIS ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 527$  (36890), 509 (37235  $M^{-1} cm^{-1}$ );  $\phi_F = 0.98 \pm 0.05$ ;  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  8.53-8.25 (m, 2 H); 7.58 (m, 4 H); 7.38 (m, 4 H); 7.31-6.75 (m, broad, 110 H); 2.61 (sept.,  $^3J = 6.60$  Hz, 1 H); 1.11 (d,  $^3J = 6.60$  Hz, 12 H);  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  164.19 (q, C=O); 145.87 (q); 143.84 (q); 142.03 (q); 141.90 (q); 141.27 (q); 141.16 (q); 140.93 (q); 140.80 (q); 140.67 (q); 140.55 (q); 140.35 (q); 140.20 (q); 139.79 (q); 139.35 (q); 138.61 (q); 138.43 (q); 138.10 (q); 133.03 (t); 132.47 (q); 132.28 (t); 131.97 (t); 131.46 (q); 130.63 (q); 130.59 (t); 130.17 (t); 129.68 (t); (q); 128.09 (t); 128.27 (q); 127.93 (t); 127.41 (t); 126.98 (t); 126.65 (t); 125.70 (t); 124.23 (t); 123.89 (t); 121.14 (q); 120.99 (q); 120.43 (t); 120.42 (t); 29.79 (t); 24.14 (t) MS (FD, 8kV) m/z (%): 2322 (100 %) [ $M^+$ ]; Anal. Calcd. for  $C_{179}H_{125}NO_2$ : C, 92.59; H, 5.43, N, 0.60; Found: C, 92.32; H, 5.31, N, 0.61;

**25b:** **25b** was prepared analogously to **25a** starting from **24b** (0.12 g, 0.06 mmol) and **14** (0.055 g, 0.14 mmol) in 2 ml o-xylene to give **25b** as a red powder (163 mg, 97 %); mp: > 300°C, UV/VIS ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 527$  (73820), 509 (74547  $M^{-1} cm^{-1}$ );  $\phi_F = 0.98 \pm 0.05$ ;  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  8.55-8.22 (m, 4 H); 7.55 (m, 8 H); 7.34-6.62 (m, broad, 110 H); 2.76 (sept.,  $^3J = 6.60$  Hz, 4 H); 1.16 (d,  $^3J = 6.60$  Hz, 24 H),  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  164.36 (q, C=O); 145.52 (q); 144.67 (q); 143.89 (q); 142.21 (q); 142.00 (q); 141.74 (q); 141.44 (q); 141.16 (q); 141.04 (q); 140.93 (q); 140.89 (q); 140.52 (q); 140.49 (q); 140.36 (q); 140.20 (q); 139.85 (q); 139.46 (q); 139.35 (q); 139.02 (q); 138.64 (q); 138.43 (q); 138.19 (q); 137.96 (q); 133.81 (t); 132.77 (q); 132.27 (t); 132.19 (t); 131.87 (t); 131.48 (q); 130.93 (q); 130.50 (t); 130.37 (t); 129.64 (t); 129.58 (q); 128.57 (t); 128.45 (q); 127.83 (t); 127.46 (t); 126.65 (t); 125.51 (t); 123.97 (t); 120.63 (q); 120.57 (t); 120.42 (t); 29.16 (t) 24.87 (t); MS (FD, 8kV) m/z (%): 2801 (100 %) [ $M^+$ ]; 1400 (11 %) [ $M^{2+}$ ]. Anal. Calcd. for  $C_{213}H_{150}N_2O_4$ : C, 91.32; H, 5.40, N, 1.00; Found: C, 91.82; H, 5.38, N, 0.93;

**25c:** **25c** was prepared analogously to **25a** starting from **24c** (0.15 g, 0.05 mmol) and **14** (0.025 g, 0.065 mmol) in 2 ml o-xylene to give **25c** as a red powder (0.15 mg, 91 %); mp: > 300°C, UV/VIS ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 527$  (111256), 509 (112352  $M^{-1} cm^{-1}$ );  $\phi_F = 0.98 \pm 0.05$ ;  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  8.61-8.58 (m, 6 H); 8.45-8.43 (m, 12 H); 7.68-6.83 (m, broad, 105 H); 6.76 (m, 8 H); 2.77 (sept.,  $^3J = 6.60$  Hz, 8 H); 1.16 (d,  $^3J = 5.50$  Hz, 36 H);  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  164.15 (q, C=O); 145.87 (q); 144.64 (q); 143.84 (q); 142.03 (q); 141.90 (q); 141.66 (q); 141.27 (q); 141.03 (q); 140.80 (q); 140.67 (q); 140.35 (q);

140.20 (q); 139.78 (q); 139.44 (q); 139.35 (q); 138.95 (q); 138.36 (q); 138.17 (q); 138.00 (q); 133.39 (t); 132.62 (q); 132.26 (t); 131.91 (t); 131.56 (t); 131.48 (q); 130.75 (q); 130.49 (t); 130.30 (t); 129.41 (t); 129.21 (q); 128.98 (t); 128.56 (t); 128.30 (q); 128.25 (q); 127.93 (t); 127.41 (t); 126.98 (t); 126.65 (t); 125.70 (t); 124.23 (t); 123.89 (t); 120.98 (q); 120.86 (q); 120.52 (t); 120.31 (t); 29.35 (t); 24.35 (t). Anal. Calcd. for  $C_{247}H_{175}N_3O_6$ : C, 90.42; H, 5.38, N, 1.28; Found: C, 90.89; H, 5.43, N, 1.28;

**25d:** **25d** was prepared analogously to **25a** starting from **1** (0.042 g, 0.101 mmol) and **6** (0.7 g, 0.81 mmol) in 2 ml *o*-xylene to give **25d** as a red powder (0.341 g, 90%); mp: > 300°C, UV/VIS ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = 527 (148424), 508 (142379 M^{-1} cm^{-1})$ ;  $\phi_F = 0.98 \pm 0.05$ ;  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  8.55-8.22 (m, broad, 24 H); 7.56 (m, 4 H); 7.38 (m, 8 H); 7.25-6.60 (m, broad, 104 H); 2.61 (sept.,  $^3J = 6.60$  Hz, 8 H); 1.06 (d,  $^3J = 6.60$  Hz, 48 H),  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  164.15 (q, C=O); 145.87 (q); 144.64 (q); 143.84 (q); 142.03 (q); 141.90 (q); 141.66 (q); 141.27 (q); 141.16 (q); 141.03 (q); 140.93 (q); 140.80 (q); 140.67 (q); 140.55 (q); 140.35 (q); 140.20 (q); 139.78 (q); 139.44 (q); 139.35 (q); 138.95 (q); 138.64 (q); 138.36 (q); 138.17 (q); 138.00 (q); 133.39 (t); 132.62 (q); 132.26 (t); 131.91 (t); 131.56 (t); 131.48 (q); 130.75 (q); 130.49 (t); 130.30 (t); 129.41 (t); 129.21 (q); 128.98 (t); 128.56 (t); 128.30 (q); 128.25 (q); 127.93 (t); 127.41 (t); 126.98 (t); 126.65 (t); 125.70 (t); 124.23 (t); 123.89 (t); 120.98 (q); 120.86 (q); 120.52 (t); 120.31 (t); 29.27 (t); 24.17 (t); MALDI-TOF:  $m/z = 3759.8 (100\%) [M^+]$  (cal. 3760.7). Anal. Calcd. for  $C_{281}H_{200}N_4O_8$ : C, 89.75; H, 5.36, N, 1.49 Found: C, 89.44; H, 5.30, N, 1.41

**25e:** **24c** (0.046 g, 0.016 mmol) and **12** (0.033 g 0.024 mmol) in 2 ml *o*-xylene/DMSO (1:1) were heated 12 h at 190°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting first with  $CH_2Cl_2$  and thereafter with acetone until unreacted **12** was separated. **25e** was washed from the column with THF to give **25e** (27 mg, 39 %) as a purple powder; mp: > 300°C, UV/VIS ( $CHCl_3$ ):  $\lambda_{max}(\epsilon) = \lambda_{max}(\epsilon) = 700 (83613), 527 (111256), 508 (112352), 225 nm (926700 M^{-1} cm^{-1})$ ;  $\phi_F = 0.98 \pm 0.05$ ;  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  9.77 (d,  $^3J = 8.76$ , 1 H); 8.65 (d;  $^3J = 8.97$ , 1 H); 8.07 (d,  $^3J = 8.01$ , 1 H); 7.90 (s, 1 H); 7.82-7.70 (m, 4 H); 7.65 (m, 2 H); 7.56 (d,  $^3J = 8.01$ , 2 H); 7.30-6.7 (m, 138 H); 6.65-6.62 (m, 4 H); 6.49-6.46 (m, 3 H); 2.48 (sept.,  $^3J = 6.5$ , 8 H); 1.23 (s, 9 H); 1.18 (d,  $^3J = 6.7$  Hz, 48 H) 1.04 (s, 9 H);  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  187.12 (C=O); 164.3; 163.52; 146.84; 145.65; 144.01; 142.84; 14.74; 142.31; 142.18; 141.93; 141.82; 141.54; 141.16; 140.71; 140.44; 140.01; 138.40; 138.23; 137.93; 133.61; 132.34; 131.34; 131.73; 131.39; 130.99; 130.84; 130.28; 129.97; 129.81; 129.59; 129.35; 129.19; 128.70; 128.45; 128.08; 127.9; 127.80; 127.26; 126.54; 126.32; 124.92; 124.54; 122.23; 122.10; 121.41; 121.19; 119.06; 55.77; 35.10; 31.81; 29.93; 24.28; MALDI-TOF:  $m/z = 4283 [M^+]$  (cal. 4283); 4391 [ $M^+Ag$ ].

**26a:** **2** (0.2 g, 0.35 mmol) and **17** (1.5 g, 1.3 mol) in 20 ml *o*-xylene were heated for 4 days at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting with  $CH_2Cl_2/PE$  (1:1,  $R_f$ : 0.92) to give **26a** as a colorless powder (0.96 g, 70 %); mp: > 300°C,  $^1H$ -NMR (300 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  7.51 (s, 3H), 7.43 (s, 3H), 7.43 (s, 3H), 7.35-7.30 (m, 2H), 7.17-7.06 (m, 48 H); 6.99-6.65 (m, 128 H); 6.59-6.55 (m, 13 H), 1.01 (m, 21 H);  $^{13}C$ -NMR (75 MHz,  $CD_2Cl_2$ , 293 K):  $\delta$  146.71; 144.63; 142.15; 142.15; 142.78; 141.82; 141.03; 141.00; 140.89; 140.75; 140.66; 140.41; 140.21; 140.07; 139.63; 137.59; 139.33; 139.25; 139.21; 138.86; 132.14; 131.96; 131.46; 130.57; 130.31; 129.13; 128.92; 128.69; 127.93; 127.14; 126.87; 126.64; 125.78; 125.51; 108.79; 91.43; 19.77; 12.03; MALDI-TOF:  $m/z = 3925 [M^+]$  (cal. 4283); 4033 [ $M^+Ag$ ]; Anal. calc. for  $C_{306}H_{220}Si$ : C, 93.64; H, 5.65, N, 0.72; Found: C, 93.44; H, 5.30, N, 0.78;



**26b:** **3** (0.08 g, 0.11 mmol) and **6** (0.371 g, 0.13 mmol) in 2 ml o-xylene were used. **26b** was obtained after column chromatography CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2, R<sub>f</sub>: 0.62) to give **26b** (0.306 g, 93%), mp. > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 7.52 (s, 2 H), 7.43 (s, 2 H), 7.40 (s, 2 H), 7.45-7.43 (d, <sup>3</sup>J = 9, 4 H); 7.15 (m, 32 H); 7.02-6.68 (m, 88 H), 6.6-6.51 (m, 8 H); 1.1 (s, 42 H); <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 147.95; 144.40; 142.68; 142.59; 142.50; 141.89; 141.51; 141.39; 141.23; 141.17; 141.01; 140.84; 140.35; 139.99; 139.66; 139.33; 138.97; 138.68; 132.50; 132.30; 131.79; 130.68; 129.86; 129.39; 129.13; 128.27; 127.54; 127.24; 126.96; 126.29; 126.02; 120.58; MS (FD, 8kV) m/z (%) 2964 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>227</sub>H<sub>180</sub>Si<sub>2</sub>: C, 91.30; H, 9.12; Found: C, 91.44; H, 9.30;

**26c:** **4** (0.088 mg 0.1 mmol) and **6** (0.171 g, 0.085 mmol) in 2 ml o-xylene were used. **26c** was obtained after column chromatography CH<sub>2</sub>Cl<sub>2</sub>/PE (1:4, R<sub>f</sub>: 0.46) to give **26c** (0.19 mg 95%); mp. > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 7.50 (s, 1 H), 7.42 (s, 1 H), 7.38 (s, 1 H), 7.35-7.33 (m, 7 H), 7.20-6.66 (m, 64 H); 6.57-6.49 (m, 4 H); 1.12 (s, 63 H), <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 142.32; 142.13; 141.12; 140.65; 139.29; 132.11; 131.93; 131.60; 131.48; 131.19; 130.33; 129.69; 129.03; 128.75; 128.01; 127.9; 127.21; 126.87; 126.59; 125.94; 121.71; 119.23; 107.32; 91.29; 18.83; 11.76; MS (FD, 8kV) m/z (%) 2003 (100 %) [M<sup>+</sup>]. Anal. Calcd. for C<sub>148</sub>H<sub>140</sub>Si<sub>3</sub>: C, 88.75; H, 7.05; Found: 88.71; H, 7.01;

**27a:** **27a** was prepared analogously to **24a** starting from **23a** (0.96 g, 0.24 mmol), NH<sub>4</sub>F (0.02 g, 0.54 mmol) and 30 ml THF to give **27a** as a colorless powder (0.81 mg, 94 %); mp. > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 7.52 (s, 3H), 7.44 (s, 3H), 7.40 (s, 3H), 7.34-7.31 (m, 2H), 7.17-7.08 (m, 48 H); 6.99-6.67 (m, 128H); 6.59-6.513 (m, 13 H), 3.12 (s, 1H); <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 146.2; 144.45; 142.32; 142.25; 142.15; 141.53; 141.13; 141.04; 140.89; 140.82; 140.65; 140.49; 140.17; 139.99; 139.64; 137.57; 139.30; 139.31; 139.29; 138.97; 132.13; 131.95; 131.46; 130.57; 130.32; 129.29; 129.04; 128.78; 127.91; 127.18; 126.88; 126.61; 125.94; 125.66; 82.11; 78.34; MS (FD, 8kV) m/z (%) 3768 (100 %) [M<sup>+</sup>]. Anal. Calcd for C<sub>297</sub>H<sub>200</sub>: C, 94.65; H, 5.35, N, 0.60 Found: C, 91.99; H, 5.52

**27b:** **27b** was prepared analogously to **24a** starting from **23b** (0.25 g, 0.08 mmol) and NH<sub>4</sub>F (0.0125 g, 0.337 mmol) in 9 ml THF to give (0.197 g, 92 %) **27b** as a colorless solid; mp: > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 7.52 (s, 2 H), 7.44 (s, 2 H), 7.40 (s, 2H), 7.46-7.43 (d, <sup>3</sup>J = 9, 4 H); 7.15 (m, 32 H); 7.02-6.67 (m, 88 H), 6.6-6.51 (m, 8 H); 3.12 (s, 2 H); <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 147.95; 144.40; 142.68; 142.59; 142.50; 141.89; 141.51; 141.39; 141.23; 141.17; 141.01; 140.84; 140.35; 139.99; 139.66; 139.33; 138.97; 138.68; 132.50; 132.30; 131.79; 130.68; 129.86; 129.39; 129.13; 128.27; 127.54; 127.24; 126.96; 126.29; 126.02; 120.58; MS (FD, 8kV) m/z (%) 2651 (100 %) [M<sup>+</sup>]. Anal. Calcd for C<sub>209</sub>H<sub>140</sub>: C, 94.68; H, 5.32; Found: C, 94.13; 5.23;

**27c:** **27c** was prepared analogously to **24a** starting from **23c** (0.15 g, 0.075 mmol) and NH<sub>4</sub>F (0.0167 mg, 0.45 mmol) in 7 ml THF. **27c** (0.11 g, 93 %) was obtained as a colorless solid, mp: > 300°C; <sup>1</sup>H-NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 7.75 (s, 1 H); 7.68 (s, 1 H); 7.63-7.60 (m, 8 H); 7.51-7.92 (s, 63 H); 6.82-6.75 (m, 4 H); 3.36 (s, 3 H); <sup>13</sup>C-NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 147.60; 144.05; 142.32; 142.23; 142.14; 141.54; 141.15; 141.04; 140.88; 140.82; 140.65; 140.49; 140.00; 139.63; 139.30; 138.98; 138.62; 138.32; 132.15; 131.95; 131.44; 130.32; 129.51; 129.04; 128.78; 127.9; 127.18; 126.89; 126.60; 125.94; 125.66; MS (FD, 8kV) m/z (%) 1534 (100 %, M<sup>+</sup>), 768 (18 %, M<sup>2+</sup>). Anal. Calc. for C<sub>121</sub>H<sub>80</sub>: C, 94.74; H, 5.26; Found: C, 94.19; 5.33;

**28a:** **27a** (0.077 g, 0.02 mmol) and **22** (0.055 g, 0.034 mol) in 2 ml o-xylene were heated for 3 days at 170°C under an argon atmosphere. The reaction mixture was evaporated to dryness and the crude product was purified by chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> (R<sub>f</sub>: 0.92) to give **28a** as a bright red powder (0.095 g, 88 %), mp: > 300°C,  $\phi_F = 0.98 \pm 0.05$ ; <sup>1</sup>H-NMR (500 MHz, THF, 293 K):  $\delta$  8.65-8.57 (m, broad, 6 H); 7.59-7.35 (m, 24 H); 7.31-6.65 (m, 219 H); 6.62-6.50 (m, 20 H); 2.80 (sept., <sup>3</sup>J = 6.60 Hz, 2 H); 1.15 (d, <sup>3</sup>J = 7 Hz, 14 H), <sup>13</sup>C-NMR (75 MHz, THF, 293 K):  $\delta$  164.33 (q, C=O); 146.88 (q); 145.52 (q); 142.92 (q); 142.79 (q); 141.81 (q); 141.52 (q); 141.18 (q); 141.15 (q); 141.01 (q); 140.67 (q); 140.63 (q); 140.23 (q); 140.15 (q); 140.08 (q); 139.89 (q); 139.64 (q); 139.58 (q); 139.24 (q); 138.92 (q); 138.52 (q); 138.37 (q); 138.12 (q); 136.93 (q); 132.68 (t); 132.56 (t); 132.57 (t); 132.45 (t); 132.10 (t); 131.92 (t); 131.48 (q); 131.25 (t); 130.91 (t); 130.72 (t); 130.37 (q); 130.12 (t); 129.31 (t); 128.27 (t); 127.90 (q); 127.68 (t); 127.60 (t); 127.311 (t); 126.92 (t); 126.52 (t); 126.37 (t); 126.27 (t); 126.02 (t); 124.28 (t); 122.29 (q); 122.17 (q); 29.98 (t); 24.27 (t); MALDI-TOF: m/z = 5365 [M<sup>+</sup>] (cal. 5365). Anal. Calcd. for C<sub>419</sub>H<sub>285</sub>NO<sub>2</sub>: C, 93.79; H, 5.35, N, 0.26 Found: C, 93.21; H, 5.42, N, 0.59

**28b:** **27b** (0.05 g, 0.019 mmol) and **22** (0.06 g, 0.037 mmol) in 2 ml o-xylene were used. Column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1.5:1, R<sub>f</sub>: 0.62) gave **28b** (0.07 mg, 63%) as a bright red powder; mp: > 300°C;  $\phi_F = 0.98 \pm 0.05$ ; <sup>1</sup>H-NMR (500 MHz, THF, 293 K):  $\delta$  8.67-8.58 (m, broad, 12 H); 7.31-6.50 (m, 245 H); 2.78 (sept., <sup>3</sup>J = 6.60 Hz, 4 H); 1.1 (d, <sup>3</sup>J = 7.1 Hz, 24 H), <sup>13</sup>CNMR (75 MHz, THF, 293 K):  $\delta$  164.21 (q, C=O); 146.92 (q); 145.04 (q); 143.18 (q); 142.72 (q); 141.79 (q); 141.53 (q); 141.35 (q); 141.00 (q); 140.98 (q); 140.64 (q); 140.68 (q); 140.23 (q); 140.17 (q); 140.08 (q); 139.93 (q); 139.64 (q); 139.78 (q); 139.24 (q); 138.92 (q); 138.52 (q); 138.37 (q); 138.12 (q); 136.93 (q); 132.68 (t); 132.63 (t); 132.57 (t); 132.45 (t); 132.10 (t); 131.92 (t); 131.48 (q); 131.25 (t); 130.91 (t); 130.72 (t); 130.37 (q); 130.12 (t); 129.31 (t); 128.27 (t); 127.90 (q); 127.68 (t); 127.60 (t); 127.311 (t); 126.92 (t); 126.52 (t); 126.37 (t); 126.27 (t); 126.02 (t); 124.28 (t); 122.29 (q); 122.17 (q); 29.81 (t) 24.21 (t); MALDI-TOF: m/z = 5845 [M<sup>+</sup>] (cal. 5845). Anal. Calcd. for C<sub>453</sub>H<sub>310</sub>N<sub>2</sub>O<sub>4</sub>: C, 93.08; H, 5.35, N, 0.48; Found: C, 93.29; H, 5.34; N, 0.42;

**28c:** **27c** (0.027 g, 0.018 mmol) and **22** (0.129 g, 0.079 mmol) in 2 ml o-xylene were used. Column chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> (R<sub>f</sub>: 0.41) gave (0.091 g, 80 %) of **28c** as a bright red powder, mp > 300°C;  $\phi_F = 0.98 \pm 0.05$ ; <sup>1</sup>H-NMR (500 MHz, THF, 293 K):  $\delta$  8.61-8.58 (m, 18 H); 7.61-6.68 (m, 24 H); 7.61-6.65 (m, 238 H); 6.63-6.50 (m, 12 H); 2.79 (sept., <sup>3</sup>J = 6.60 Hz, 2 H); 1.14 (d, <sup>3</sup>J = 7 Hz, 42 H), <sup>13</sup>C-NMR (75 MHz, THF, 293 K):  $\delta$  164.32 (q, C=O); 145.55 (q); 144.13 (q); 142.92 (q); 142.79 (q); 142.00 (q); 141.87 (q); 141.82 (q); 141.76 (q); 141.66 (q); 141.52 (q); 141.39 (q); 141.25 (q); 141.18 (q); 141.02 (q); 140.68 (q); 140.25 (q); 140.16 (q); 140.09 (q); 139.91 (q); 139.82 (q); 139.51 (q); 139.38 (q); 139.25 (q); 138.92 (q); 138.48 (q); 138.33 (q); 138.13 (q); 133.73 (q); 133.73 (q); 132.69 (t); 132.65 (t); 132.58 (t); 132.44 (t); 132.11 (t); 131.46 (q); 131.26 (t); 130.92 (t); 130.72 (t); 130.36 (q); 129.56 (t); 129.35 (t); 129.26 (q); 128.46 (t); 128.29 (t); 127.68 (t); 127.60 (t); 127.31 (t); 126.91 (t); 126.38 (t); 126.28 (t); 126.02 (t); 124.90 (t); 124.57 (t); 124.27 (t); 122.30 (q); 122.17 (q); 121.45 (t); 121.22 (t); 68.21 (q); 29.98 (t); 24.26 (t); MALDI-TOF: m/z = 6325 [M<sup>+</sup>] (cal. 6325). Anal. Calcd. for C<sub>487</sub>H<sub>335</sub>N<sub>3</sub>O<sub>6</sub>: C, 92.48; H, 5.34, N, 0.66; Found: C, 93.29; H, 5.34; N, 0.42;

**28d:** **27d** (7 mg, 0.017 mmol) and **22** (0.16 mg, 0.098 mmol) in 2 ml o-xylene were used. Column chromatography with CH<sub>2</sub>Cl<sub>2</sub> (R<sub>f</sub>: 0.2) and eluting with THF gave **28d** (0.07 g, 61%) as a bright red powder, mp >300°C;  $\phi_F = 0.98 \pm 0.05$ ; <sup>1</sup>H-NMR (500 MHz, THF, 293 K):  $\delta$  8.61-8.58 (m, 24 H); 7.7-6.7 (m, 254 H); 6.55-6.52 (m, 18 H); 2.78 (sept., <sup>3</sup>J = 6.60 Hz, 8 H); 1.16 (d, <sup>3</sup>J = 7 Hz, 56 H), <sup>13</sup>C-NMR (75 MHz, THF, 293 K):  $\delta$  164.32 (q); 146.87 (q); 145.55

(q); 144.13 (q); 142.92 (q); 142.49 (q); 142.00 (q); 141.87 (q); 141.83 (q); 141.65 (q); 141.43 (q); 141.39 (q); 141.25 (q); 141.18 (q); 140.65 (q); 140.25 (q); 140.16 (q); 139.94 (q); 139.82 (q); 139.63 (q); 139.51 (q); 139.37 (q); 137.25 (q); 139.04 (q); 138.93 (q); 138.48 (q); 138.33 (q); 138.12 (q); 137.85 (q); 133.73 (q); 132.69 (t); 132.64 (q); 132.44 (q); 132.13 (q); 131.45 (t); 130.92 (q); 130.72 (q); 130.53 (t); 129.61 (q); 129.36 (q); 128.29 (q); 127.69 (q); 127.60 (q); 127.31 (q); 126.92 (q); 126.39 (q); 124.91 (q); 124.57 (q); 124.27 (q); 122.29 (t); 122.17 (t); 121.45 (q); 121.22 (q); 108.40 (t); 67.92 (t); 29.98 (t); 24.25 (t); MALDI-TOF:  $m/z = 6804 [M^+]$  (cal. 6804); Anal. Calcd. for  $C_{521}H_{360}N_4O_8$ : C, 91.96; H, 5.33, N, 0.82; Found: C, 92.21; H, 5.58, N, 0.94.