Supporting information for:

Synthesis and Optical Properties of Polyphenylene Dendrimers Based on Perylenes

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S3 Experimental section (The NMR peak assignments of compound **3** and **4**; Data and experimental details for **8**, **9**, **10**, **12**, and **13**)

Materials: Tetrahydrofuran (Fluka) was distilled over sodium/benzophenone. Tetrabutylammonium fluoride (Fluka), di(triphenylphosphine)dichloropalladium(II) (Strem), Perylene (Aldrich), trimethylethyne (Aldrich), copper(I) *p*-iodophenol (Avocado), *m*-xylene(Aldrich), were used as obtained. Column chromatography was performed with dichloromethane (chromasolv, Riedel) or toluene on silica gel (Geduran Si60, Merck). All the reported yields are isolated yields.

Physical and analytical methods: ^1H - and ^{13}C -NMR spectra were recorded by using the residual proton resonance of the solvent or the carbon signal of the deuterated solvent as the internal standard. Chemical shifts are reported in parts per million. For ^{13}C j-modulated spin-echo NMR measurements, the abbreviations q and t represent quaternary C atoms and CH_2 as well as CH_3 and CH groups, respectively. MALDI-TOF mass spectra were measured and dithranol as matrix (molar ratio dithranol/sample 250:1). The mass peaks with the lowest isotopic mass are reported. The quantum yields of polyphenylene dendronized perylenes were measured using perylene in toluene as a reference. The elemental analyses were carried out by the Microanalytical Laboratory of the Universität Mainz (Germany).

Experimental section

3,9(10)-Di(triisopropylsilylethynyl)perylene (3)

^1H -NMR Spectrum (250MHz, THF, 300K) δ [ppm]: 8.40 (d, $J = 7.5$ Hz, 2H), 8.28 (m, 4H), 7.71 (dd, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 6.8$ Hz, $J = 7.5$ Hz, 2H), 1.24 (s, 42H,

isopropyl); ^{13}C -NMR Spectrum (j-modulated spin-echo, 62.5 MHz, THF, 300K) $\delta[\text{ppm}]$: 135.8 (q), 132.8 (t), 132.7 (t), 132.4 (q), 128.5 (t), 127.6 (t), 127.2 (t), 122.9 (t), 122.5 (t), 122.0 (q), 121.7 (t), 121.2 (t), 106.8 (q, C-Perylene, ethynyl), 97.9 (q, C-Si, ethynyl), 97.7 (q, C-Si, ethynyl), 19.3 (t, CH_3 , *isopropyl*), 12.5 (t, CH, *isopropyl*).

3,9(10)-Diethynylperylene (4)

^1H -NMR Spectrum (250MHz, THF, 300K) $\delta[\text{ppm}]$: 7.69 (d, $J = 7.5$ Hz, 2H), 7.59 (dd, $J = 8.0$ Hz, 2H), 7.54 (dd, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 7.5$ Hz, 2H), 6.90 (t, $J = 7.5$ Hz, 2H), 3.42 (s, 1H, ethynyl), 3.40 (s, 1H, ethynyl); ^{13}C -NMR Spectrum (62.5 MHz, THF, 300K) $\delta[\text{ppm}]$: 135.7, 132.6, 132.5, 132.3, 129.0, 128.3, 127.3, 126.9, 122.6, 122.2, 121.4, 121.1, 121.0, 120.8, 85.2 (C-perylene, ethynyl), 85.1 (C-perylene, ethynyl), 82.5 (CH, ethynyl).

3,9(10)-bis[(2,5-phenyl-3,4-triisopropylsilyl)ethynylphenyl]perylene (8)

As for **6**, perylene derivative **4** (200 mg, 0.667 mmol), tetraphenylcyclopentadienone derivative **7** (1.49 g, 2.0 mmol) and *m*-xylene (5 ml) were used to give a yellow solid **8** (1.02 g, 89%). $R_f = 0.4$ (CH_2Cl_2 : hexane 1:5); $\text{Mp} > 300^\circ\text{C}$; ^1H -NMR Spectrum (250MHz, THF, 300K) $\delta[\text{ppm}]$: 8.16 (m, 2H), 8.00 (m, 2H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.50 (t, $J = 8.0$ Hz, 2H), 7.19-7.08 (m, 16H), 7.03 (m, 4H), 6.91 (s, 12 H), 6.85 (m, 14H), 6.71 (m, 4H), 1.10 (d, $J = 5.6$ Hz, 84H, *isopropyl*); ^{13}C -NMR Spectrum (62.5 MHz, THF, 300K) $\delta[\text{ppm}]$: 142.3; 142.0, 141.8, 141.7, 141.6, 141.4, 140.8, 140.7, 140.5, 139.8, 139.6, 134.4, 133.4, 133.2, 132.5, 132.4, 132.3, 131.9, 131.6, 131.3, 131.2, 131.0, 130.7, 129.9, 129.3, 128.5, 127.3, 127.1, 126.6, 121.7, 121.4, 121.0, 120.3, 120.1, 108.5 (C-Ph, ethynyl), 90.3 (C-Si, ethynyl), 90.0 (C-Si, ethynyl), 19.0 (CH_3 , *isopropyl*), 12.2 (CH,

isopropyl); IR Spectrum (KBr) ν = 2942, 2891, 2863, 2361, 2335, 2152, 1644, 1504, 1462, 1385, 1220, 1102, 1073, 1017, 996, 917, 882, 831, 761, 675, 576, 466 cm^{-1} ; UV-Vis Spectrum (Chloroform) λ_{max} = 434 (36824), 462 nm (45375 $\text{M}^{-1}\text{cm}^{-1}$); Fluorescence Spectrum (Chloroform) λ_{max} = 484, 512 nm (excitation 430 nm); FD Mass Spectrum (8kV): m/z = 1734 (100%) [M^+] (Calc. 1734); Anal. Calcd. (%) for ($\text{C}_{124}\text{H}_{132}\text{Si}_4$): C 85.85, H 7.67; found: C 85.23, H 7.92.

3,9(10)-bis[(2,5-phenyl-3,4-ethynylphenyl)phenyl]perylene (9)

As for **4**, trialkylsilyl derivative **8** (500 mg, 0.286 mmol), *n*-tetrabutylammonium fluoride (530 mg, 1.72 mmol) and THF (50 ml) were used to give a yellow solid **9** (290 mg, 92%). R_f = 0.89 (CHCl_3); Mp > 300 °C; ^1H -NMR Spectrum (250MHz, THF, 300K) δ [ppm]: 8.15 (m, 2H), 8.04 (m, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.60 (m, 2H), 7.53 (t, J = 8.0 Hz, 2H), 7.42-7.28 (m, 4H), 7.21-7.06 (m, 12H), 6.99 (d, J = 8.0 Hz, 4H), 6.82 (m, 14H), 6.71 (m, 4H), 3.42 (s, 2H, ethynyl), 3.37 (s, 2H, ethynyl); ^{13}C -NMR Spectrum (62.5 MHz, THF, 300K) δ [ppm]: 142.2; 142.0, 141.8, 141.6, 141.5, 140.7, 140.5, 139.8, 139.6, 134.4, 133.2, 132.5, 132.4, 132.3, 131.9, 131.6, 131.3, 131.1, 130.7, 129.9, 129.4, 128.5, 127.9, 127.7, 127.5, 127.2, 127.1, 126.6, 121.7, 121.0, 120.7, 120.3, 84.2 (C-Ph, ethynyl), 78.7 (CH, ethynyl), 78.5 (CH, ethynyl); IR Spectrum (KBr) ν = 3292, 2922, 2361, 2336, 1644, 1504, 1436, 1389, 1106, 843, 811, 757, 700, 651, 552 cm^{-1} ; UV-Vis Spectrum (Chloroform) λ_{max} = 434 (37278), 473 nm (46235 $\text{M}^{-1}\text{cm}^{-1}$); Fluorescence Spectrum (Chloroform) λ_{max} = 484, 513 nm (excitation 430 nm); FD Mass Spectrum (8kV): m/z = 1109 (100%) [M^+] (Calc. 1109); Anal. Calcd. (%) for ($\text{C}_{88}\text{H}_{52}$): C 95.28, H 4.72; found: C 95.19, H 4.80.

16-cascade:perylene[2-3,9(10)]:(2,3,4,5-phenylene):(1,2,3,4,5-phenylene):benzene (10)

A mixture of **9** (100 mg, 0.090 mmol) and tetraphenylcyclopentadienone **5** (210 mg, 0.603 mmol) in *m*-xylene (3 ml) were stirred at 170 °C for 48 h under Argon. The cooled reaction mixture was added to 100 ml of methanol to give a precipitate. The product was purified by column chromatography to give a yellow solid (195 mg, 85%). $R_f = 0.92$ (CH_2Cl_2); $\text{Mp} = 310.8\text{ }^\circ\text{C}$; $^1\text{H-NMR}$ Spectrum (250MHz, THF, 300K) $\delta[\text{ppm}]$: 8.15 (m, 2H), 8.02 (m, 2H), 7.66 (d, $J = 8.0\text{ Hz}$, 2H), 7.47 (s, 4H), 7.40 (s, 2H), 7.33 (m, 2H), 7.10 (dd, $J = 7.5\text{ Hz}$, 32H), 6.98-6.68 (m, 78H), 6.57 (m, 8H); $^{13}\text{C-NMR}$ Spectrum (j-modulated spin-echo, 62.5 MHz, THF, 300K) $\delta[\text{ppm}]$: 142.9 (q), 142.8 (q), 141.8 (q), 141.5 (q), 141.4 (q), 141.3 (q), 141.1 (q), 140.2 (q), 140.1 (q), 140.0 (q), 139.9 (q), 139.5 (q), 138.8 (q), 132.4 (t), 132.1 (t), 131.9 (t), 130.9 (t), 130.6 (t), 129.6 (t), 129.3 (q), 128.3 (t), 127.6 (t), 127.3 (t), 126.9 (t), 126.3 (t), 126.0 (t); IR Spectrum (KBr) $\nu = 3054, 2361, 2336, 1600, 1497, 1436, 1384, 1076, 1026, 903, 842, 761, 699, 672, 550\text{ cm}^{-1}$; UV-Vis Spectrum (Chloroform) $\lambda_{\text{max}} = 272$ (222620), 422 (21323), 444 (44785), 471 nm (55459 $\text{M}^{-1}\text{cm}^{-1}$); Fluorescence Spectrum (Chloroform) $\lambda_{\text{max}} = 485, 514\text{ nm}$ (excitation 440 nm); MALDI-TOF Mass Spectrum: $m/z = 2535$ (100%) [M^+] (Calc.2535); Anal. Calcd. (%) for ($\text{C}_{200}\text{H}_{132}$): C 94.75, H 5.25; found: C 94.39, H 5.32.

8-cascade:perylene[2-3,9(10)]:(2,3,4,5-phenylene):triisopropylsilylacetylene (12)

As for **6**, perylene derivative **4** (100 mg, 0.333 mmol), tetraphenylcyclopentadienone derivative **11** (1.10 g, 1.0 mmol) and *m*-xylene (6 ml) were used to give a yellow solid **12** (695 mg, 85%). $R_f = 0.3$ (CH_2Cl_2 : hexane 1:7); $\text{Mp} > 300\text{ }^\circ\text{C}$; $^1\text{H-NMR}$ Spectrum (250MHz, THF, 300K) $\delta[\text{ppm}]$: 8.08-7.82 (m, 4H), 7.57-7.44 (m, 4H), 7.29 (m, 2H), 7.14

(m, 2H), 7.08 (m, 4H), 6.95 (d, $J = 7.5$ Hz, 8H), 6.87 (d, $J = 7.5$ Hz, 6H), 6.74 (d, $J = 7.5$ Hz, 8H), 6.67 (d, $J = 7.5$ Hz, 8H), 0.92-0.80 (m, 168H, *isopropyl*); ^{13}C -NMR Spectrum (62.5 MHz, THF, 300K) δ [ppm]: 142.5; 142.2, 141.2, 141.0, 140.8, 139.7, 139.3, 134.4, 133.4, 132.4, 132.3, 131.8, 131.5, 131.3, 130.7, 130.0, 129.9, 129.4, 129.3, 127.3, 126.8, 122.5, 122.0, 121.8, 121.7, 121.2, 120.5, 120.4, 108.4 (C-Ph, ethynyl), 108.3 (C-Ph, ethynyl), 90.9 (C-Si, ethynyl), 90.6 (C-Si, ethynyl), 90.4 (C-Si, ethynyl), 90.3 (C-Si, ethynyl), 19.0 (CH_3 , *isopropyl*), 12.2 (CH, *isopropyl*); IR Spectrum (KBr) $\nu = 2942, 2891, 2863, 2361, 2335, 2153, 1642, 1506, 1463, 1385, 1222, 1105, 1070, 1015, 995, 918, 882, 831, 763, 675, 576, 511\text{ cm}^{-1}$; UV-Vis Spectrum (Chloroform) $\lambda_{\text{max}} = 435(39841), 462\text{ nm}$ ($48878\text{ M}^{-1}\text{cm}^{-1}$); Fluorescence Spectrum (Chloroform) $\lambda_{\text{max}} = 484, 514\text{ nm}$ (excitation 430 nm); FD Mass Spectrum (8kV): $m/z = 2456$ (100%) [M^+] (Calc. 2456); Anal. Calcd. (%) for ($\text{C}_{168}\text{H}_{212}\text{Si}_8$): C 82.15, H 8.70; found: C 82.24, H 8.79.

8-cascade:perylene[2-3,9(10)]:(2,3,4,5-phenylene):acetylene (13)

As for **4**, trialkylsilyl derivative **12** (500 mg, 0.203 mmol), *n*-tetrabutylammonium fluoride (630 mg, 2.03 mmol) and THF (50 ml) were used to give a yellow solid **13** (220 mg, 90%). $R_f = 0.84$ (CHCl_3); $\text{Mp} > 300\text{ }^\circ\text{C}$; ^1H -NMR Spectrum (250MHz, THF, 300K) δ [ppm]: 8.21 (m, 2H), 8.07 (m, 2H), 7.67 (m, 2H), 7.55 (m, 2H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.26 (dd, $J = 8.0$ Hz, 4H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.14 (m, 8H), 7.03 (d, $J = 7.5$ Hz, 4H), 6.93-6.81 (m, 16H), 3.50 (s, 2H, ethynyl), 3.46 (s, 2H, ethynyl), 3.41 (s, 2H, ethynyl), 3.30 (s, 1H, ethynyl), 3.28 (s, 1H, ethynyl); ^{13}C -NMR Spectrum (62.5 MHz, THF, 300K) δ [ppm]: 142.4, 142.2; 142.1, 141.3, 141.0, 140.8, 140.7, 139.7, 139.4, 137.3, 135.8, 134.3, 133.4, 133.2, 132.5, 132.2, 131.8, 131.4, 131.2, 130.7, 129.9, 129.4, 127.3, 127.0, 121.8,

121.3, 121.0, 120.4, 120.3, 84.1 (C-Ph, ethynyl), 79.2 (CH, ethynyl), 78.9 (CH, ethynyl), 78.8 (CH, ethynyl), 78.7 (CH, ethynyl); IR Spectrum (KBr) $\nu = 3289, 2361, 2336, 1633, 1505, 1391, 1105, 1015, 832, 762, 663, 617, 540 \text{ cm}^{-1}$; UV-Vis Spectrum (Chloroform) $\lambda_{\text{max}} = 435 (33671), 463 \text{ nm} (41858 \text{ M}^{-1}\text{cm}^{-1})$; Fluorescence Spectrum (Chloroform) $\lambda_{\text{max}} = 484, 512 \text{ nm}$ (excitation 430 nm); FD Mass Spectrum (8kV): $m/z = 1205 (100\%) [\text{M}^+]$ (Calc. 1205); Anal. Calcd. (%) for ($\text{C}_{96}\text{H}_{52}$): C 96.65, H 4.35; found: C 96.42, H 4.41.