Supplementary information

Highly π electron-rich macro-aromatics: bis(*p*-aminophenyl)-*carbo*-benzenes and their DBA acyclic references

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Experimental section.

General. THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane and dichloromethane over P_2O_5. All other reagents were used as commercially available. In particular, commercial solutions of *n*-BuLi were 2.5 M in hexane, solutions of ethylmagnesium bromide were 3 M in THF, solutions of HCl were 2 M in diethylether. Previously described procedures were used for the preparation of **2** and **10**.[12] All reactions were carried out under nitrogen or Argon using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 P, 70-200 mm). Silica gel thin–layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20 %). The following analytical instruments were used. ^1H and ^{13}C NMR: Bruker DPX 300, Avance 300, Avance 400, Avance 400WB or Avance 500 spectrometers. Mass spectrometry: Quadrupolar Nermag R10-10H spectrometer. Most of the NMR spectra were recorded in $CDCl_3$ solutions. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz. UV: spectrometer Perkin-Elmer UV-Vis Win-Lab Lambda 35. Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 controlled by GPES 4.09 software. Experiments were performed at room temperature in a home-made airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter) or a glassy carbon microdisk (1 mm diameter). The supporting electrolyte (n-Bu_4N)[PF_6] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in product and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Typical instrumental parameters for recorded square-wave voltammograms were: SW frequency f = 20 Hz, SW amplitude Esw = 20 mV, and scan increment dE = 0.5 mV.

4-[10-(4-aminophenyl)-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl]aniline (*p*-bis(4-aminophenyl)tetraphenyl-*carbo*-benzene) 6. A solution of *p*-bromo-N,N-bis(trimethylsilyl)aniline (0.38 mL, 1.35 mmol) in THF (1 mL) was added slowly at room temperature to a suspension of magnesium (32 mg, 1.32 mmol) in THF (0.5 mL). After the organo-magnesium derivative was formed, the resulting mixture was added to a solution of the [6]pericyclynedione **2** (150 mg, 0.22 mmol) in THF (10 mL) at 0 °C. The stirring was maintained 2 hours at 0 °C, and then overnight at room temperature. After treatment with H_2O, the aqueous layer was extracted with diethylether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The obtained poorly stable [6]pericyclynediol **3a** was directly used in the reduction step without further purification. The mixture was thus dissolved in DCM, before adding $SnCl_2$ (417 mg, 2.21 mmol) and then $HCl.Et_2O$ (2.20 mL, 4.40 mmol) at – 78 °C. The reaction mixture was allowed to warm up to room temperature slowly and the stirring was maintained one hour at RT before treating with aqueous 1 M NaOH (4.6 mL) and stirring overnight. After treatment with brine, the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography, eluting first with DCM:THF:acetone 8:1:1, then 7:1.5:1.5 then 6:2:2, then THF:acetone 1:1 to give **6**. The residue was washed with pentane to give pure **6** as a green-gold solid in 26 % yield (40 mg).

^1H NMR (THF D_8): δ = 7.23 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, m-C_6H_4-N), 7.72 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, p-C_6H_5), 8.01 (pseudo-t, $^3J_{HH}$ = 7.5 Hz, 8 H, m-C_6H_5), 9.23 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, o-C_6H_4-N), 9.47 (d, $^3J_{HH}$ = 7.5 Hz, 8 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (THF D_8): δ = 101.8 (C-C_6H_5), 105.8 (C-

C_6H_4-N), 115.1 (*m*-C_6H_4-N), 116.0, 118.2 (C=*C*=*C*=C, C-*C*≡*C*-C), 128.7 (*i*-C_6H_4-N), 128.8 (*p*-C_6H_5), 129.6 (*m*-C_6H_5), 130.0 (*o*-C_6H_5), 131.8 (*o*-C_6H_4-N), 140.4 (*i*-C_6H_5), 151.0 (*p*-C_6H_4-N). MS (MALDI-TOF/DCTB): *m/z* = 708.4 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{54}H_{32}N_2$: 708.2565, found: 708.2635. UV-vis ($CHCl_3$): λ_{max} = 493 nm (ε = 105349 L. $mol^{-1}.cm^{-1}$). M.p. = 180 °C.

4-{10-[4-(dimethylamino)phenyl]-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}-N,N-dimethylaniline (*p*-bis(4-dimethylaminophenyl)-tetraphenyl-*carbo*-benzene) 7. A solution of *p*-bromo-N,N-dimethylaniline (0.353 g, 1.76 mmol) in THF (2 mL) was added slowly at room temperature to a suspension of magnesium (43 mg, 1.76 mmol) in THF (1 mL). After the organo-magnesium derivative was formed, the resulting mixture was diluted with THF (5 mL) and was added to a solution of the [6]pericyclynedione **2** (200 mg, 0.29 mmol) in THF (10 mL) at 0 °C. The stirring was maintained 2 hours at 0 °C, and then overnight at room temperature. After treatment with H_2O, the aqueous layer was extracted with diethylether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The obtained poorly stable [6]pericyclynediol **3b** was directly used in the reduction step without further purification. The mixture was thus dissolved in diethylether (100mL), before adding $SnCl_2$ (530 mg, 2.8 mmol) and then $HCl.Et_2O$ (2.8 mL, 5.6 mmol) at – 78 °C. The reaction mixture was allowed to warm up to room temperature slowly in 5 h. and then treated with aqueous 1M NaOH (5.6 mL) and water. The aqueous layer was extracted with diethylether, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness to give a dark residue. It was purified by silica gel chromatography, eluting first with DCM:Acetone:pentane 1:1:8, then 2:2:6 then 4:4:2, then DCM:acetone 1:1, and finally with pure DCM. The poor solubility of the *carbo*-benzene **7** makes it hang on the silica gel and thus complicates a lot its purification. Pure **7** could be isolated in 6 % (15 mg) yield as a green-gold solid.

^{1}H NMR (CD_2Cl_2): δ = 3.36 (s, 12 H, N-C*H*$_3$), 7.34 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, *m*-C_6H_4-N), 7.75 (t, $^3J_{HH}$ = 8.0 Hz, 4 H, *p*-C_6H_5), 8.035 (pseudo-t, $^3J_{HH}$ = 8.0 Hz, 8 H, *m*-C_6H_5), 9.33 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, *o*-C_6H_4-N), 9.46 (d, $^3J_{HH}$ = 8.0 Hz, 8 H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 40.2 (N-*C*H$_3$), 102.1 (*C*-C_6H_5), 104.5 (*C*-C_6H_4-N), 113.0 (*m*-C_6H_4-N), 114.7, 116.0, 116.6 (C=*C*=*C*=C, C-*C*≡*C*-C), 128.9 (*i*-C_6H_4-N), 129.1 (*p*-C_6H_5), 129.8 (*m*-C_6H_5), 130.2 (*o*-C_6H_5), 131.6 (*o*-C_6H_4-N), 140.3 (*i*-C_6H_5), 151.6 (*p*-C_6H_4-N). MS (MALDI-TOF/DCTB): *m/z*: 764.4 $[M]^+$. HRMS (MALDI-TOF): *m/z* calcd for $C_{58}H_{40}N_2$: 764.3191, found: 764.3232. UV-vis ($CHCl_3$): λ_{max} = 522 nm (ε = 206472 $L.mol^{-1}.cm^{-1}$). M.p.(dec)= 300 °C.

1-(4-{10-[4-(1H-indol-1-yl)phenyl]-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}phenyl)-1H-indole (*p*-bis(4-(indol-1-yl)phenyl)-tetra-phenyl-*carbo*-benzene) 8. To the solution of the [6]pericyclynediol **4** (70 mg, 0.07 mmol) in dry dichloromethane (15mL) at -78 ˚C were added $SnCl_2$ (125 mg, 0.70 mmol) and then $HCl.Et_2O$ (0.7 mL, 0.14 mmol). The temperature of the reaction mixture was slowly increased up to -10 ˚C in 3 hours. Then aqueous 1M NaOH (1.6 mL, 0.16 mmol) was added and the mixture was allowed to warm up to room temperature. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was washed with pentane (3x20 mL) and diethylether (3x10 mL) to give pure **8** as a dark solid in 71 % yield (45 mg).

^1H NMR ($CDCl_3$): $\delta = 6.91$ (d, $^3J_{HH} = 3.2$ Hz, 2 H, H_3-indole), 7.34 (t, $^3J_{HH} = 7.2$ Hz, 2 H, H_8-indole), 7.45 (t, $^3J_{HH} = 7.2$ Hz, 2 H, H_7-indole), 7.69 (d, $^3J_{HH} = 3.2$ Hz, 2 H, H_2-indole), 7.77 (t, $^3J_{HH} = 7.2$ Hz, 4 H, p-C_6H_5), 7.86 (d, $^3J_{HH} = 7.2$ Hz, 2 H, H_6-indole), 7.98-8.04 (m, 10 H, m-C_6H_5, H_9-indole), 8.16 (d, $^3J_{HH} = 8.5$ Hz, 4 H, o-C_6H_4-N), 9.45 (d, $^3J_{HH} = 8.0$ Hz, 8 H, o-C_6H_5), 9.59 (d, $^3J_{HH} = 8.5$ Hz, 4 H, m-C_6H_4-N). $^{13}C\{^1H\}$ NMR (THF-D_8): $\delta = 104.2$ (C-C_6H_4-N), 104.6 (C-C_6H_5), 117.4, 117.6, 118.1 (C-$C{\equiv}C$-C, C=C=C=C), 120.7, 121.1, 122.6 (C_7-, C_8-, C_9-indole), 124.8 (C_2-indole), 127.7 (o-C_6H_4-N), 129.6 (p-C_6H_5), 129.9 (o-C_6H_5), 130.4 (m-C_6H_5), 131.5 (m-C_6H_4-N), 137.6, 139.9, 141.2 (i-C_6H_5, i-C_6H_4-N, p-C_6H_4-N, C_4-, C_5-indole). MS (MALDI-TOF/DCTB): m/z: 908.3 $[M]^+$. HRMS (MALDI-DCTB): m/z calcd for $C_{70}H_{40}N_2$ $[M]^+$: 908.3191, found: 908.3229. UV-vis ($CHCl_3$): $\lambda_{max} = 486$ nm ($\varepsilon = 350112$ $L.mol^{-1}.cm^{-1}$). PL ($CHCl_3$): $\lambda_{Em} = 595$ nm. M.p. > 450 °C.

9-(4-{10-[4-(9H-carbazol-9-yl)phenyl]-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyn-1-yl}phenyl)-9H-carbazole (*p*-bis(4-(carbazol-9-yl)phenyl)-tetra-phenyl-*carbo*-benzene) 9. To the solution of the [6]pericyclynediol **5** (55 mg, 0.05 mmol) in dry dichloromethane (15mL) at -78 ˚C were added $SnCl_2$ (95 mg, 0.50 mmol) and then $HCl.Et_2O$ (0.5 mL, 0.10 mmol). The temperature of the reaction mixture was slowly increased up to -10 ˚C in 3 hours. Then aqueous 1M NaOH (1.0 mL, 0.1 mmol) was added and the mixture was allowed to warm up to room temperature. The aqueous layer was extracted with DCM and combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was washed with pentane (3x20 mL) and with ether (3x10 mL) to give pure **9** as a dark solid in 69 % yield (35 mg).

^1H NMR (THF-D_8): $\delta = 7.40$ (t, $^3J_{HH} = 7.8$ Hz, 4 H, H_8-, H_{12}-carbazole), 7.58 (t, $^3J_{HH} = 7.8$ Hz, 4 H, H_7-, H_{11}-carbazole), 7.76-7.92 (m, 8 H, p-C_6H_5, H_6-, H_{10}-carbazole), 8.07 (t, $^3J_{HH} =$

7.8 Hz, 8 H, *m*-C_6H_5), 8.31 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, H_9-, H_{13}-carbazole), 8.39 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, *o*-C_6H_4-N), 9.61 (d, $^3J_{HH}$ = 7.8 Hz, 8 H, *o*-C_6H_5), 9.85 (d, $^3J_{HH}$ = 7.8 Hz, 4 H, *m*-C_6H_4-N). $^{13}C\{^1H\}$ solid NMR: δ = 102.4-111.0 (*C*-C_6H_4-N, *C*-C_6H_5, C-*C*≡*C*-C, C=*C*=*C*=C, C_6-, C_{10}-carbazole), 118.4 (*o*-C_6H_4-N, C_8-, C_{12}-carbazole), 124.5-134.8 (*o*-, *m*-, *p*-C_6H_5, *m*-C_6H_4-N, C_3-, C_4-, C_7-, C_9-, C_{11}-, C_{13}-carbazole,), 138.7 (*i*-C_6H_5, *i*-C_6H_4-N, *p*-C_6H_4-N, C_2-, C_5-carbazole). MS (MALDI-TOF/DCTB): *m/z*: 1008.4 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{78}H_{44}N_2$ $[M]^+$: 1008.3556, found: 1008.3504. UV-vis ($CHCl_3$): λ_{max} = 487 nm (ε = 288456 L.mol^{-1}.cm^{-1}). PL ($CHCl_3$): λ_{Em} = 597 nm. M.p. > 450 °C.

1,10-bis[4-(1H-indol-1-yl)phenyl]-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclo-octadeca-2,5,8,11,14,17-hexayne-1,10-diol 4. A solution of 1-(4-bromophenyl)-1H-indole (163 mg, 0.60 mmol) in THF (0.5 mL) was added to a suspension of Mg (14 mg, 0.60 mmol) in THF (0.2 mL). The reaction mixture was stirred at room temperature until Mg was completely consumed. Then mixture was diluted with THF (3 mL) and added to a solution of the [6]pericyclynedione **1** (68 mg, 0.10 mmol) in THF (5mL) at 0 ˚C. The reaction mixture was stirred 2 h. at 0 ˚C and then 16 h. at room temperature. After treatment with saturated aqueous NH_4Cl and extraction of the aqueous layer with diethylether, the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:Pentane 3:7) to give **4** as a light yellow solid in 66 % yield (70 mg). R_f (EtOAc:Heptane 3:7) = 0.14.

^1H NMR ($CDCl_3$): δ = 3.20-3.74 (m, 14 H, OCH_3, O*H*), 6.69-6.76 (m, 2 H, H_3-indole), 7.24-8.02 (m, 38 H, all the rest). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 53.6 (OCH_3), 64.8 (*C*-OH), 72.1 (*C*-OMe), 83.2, 84.7, 86.8 (C-*C*≡*C*-C), 104.2 (C_3-indole), 110.6 (C_6-indole), 120.7 (*o*-C_6H_4-N), 121.3 (C_7-, C_8-indole), 122.6 (C_2-indole), 124.1 (C_9-indole), 126.4 (*o*-C_6H_5), 127.3 (*m*-C_6H_4-N), 127.8 (C_4-indole), 128.7 (*m*-C_6H_5), 128.7 (*p*-C_6H_5), 129.3 (C_5-indole), 135.7 (*i*-C_6H_4-N), 139.3, 140.5 (*i*-C_6H_5, *p*-C_6H_4-N). MS: (MALDI-TOF/DCTB): *m/z*: 1066.5 $[M]^+$. HRMS (MALDI-DCTB): *m/z* calcd for $C_{74}H_{54}N_2O_6$ $[M]^+$: 1066.3982, found: 1066.4069. UV-vis ($CHCl_3$): λ_{max} = 268 (ε = 59609 L.mol^{-1}.cm^{-1}). PL ($CHCl_3$): λ_{Em} = 333, 481 nm. M.p. = 107 °C.

1,10-bis[4-(9H-carbazol-9-yl)phenyl]-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclo-octadeca-2,5,8,11,14,17-hexayne-1,10-diol 5. To a solution of 9-(4-bromophenyl)-9H-carbazole (90 mg, 0.28 mmol) in THF (15 mL) under stirring at -78 ˚C was added *n*-BuLi (96 µl, 0.24 mmol). The reaction mixture was stirring during 1 hour at -78 ˚C before adding a solution of the [6]pericyclynedione **1** (68 mg, 0.10 mmol) in THF (3 mL). The temperature was allowed to increase slowly up to -10 ˚C over 3 h before adding saturated aqueous NH_4Cl. The aqueous layer was extracted with diethylether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:Pentane 3:7) to give **5** as a light solid in 63 % yield (73 mg). R_f (EtOAc:Heptane 3:7) = 0.13.

^{1}H NMR ($CDCl_3$): δ = 3.26-3.71 (m, 14 H, OCH_3, O*H*), 7.36-8.21 (m, 44 H, all the rest). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 53.6 (OCH_3), 64.88 (*C*-OH), 72.1 (*C*-OMe), 83.2, 84.7, 86.80 (C-*C*≡*C*-C), 109.81 (C_6-, C_{10}-carbazole), 120.3 (*o*-C_6H_4-N), 120.4 (C_8-, C_{12}-carbazole), 123.6 (C_3-, C_4-carbazole), 126.1 (C_9-, C_{13}-carbazole), 126.6 (*o*-C_6H_5), 127.2 (C_7-, C_{11}-carbazole), 127.5 (*m*-C_6H_4-N), 128.7 (*p*-C_6H_5), 129.3 (*m*-C_6H_5), 138.5 (C_2-, C_5-carbazole), 139.4, 140.7 (*i*-C_6H_5, *i*-, *p*-C_6H_4-N). MS (MALDI-TOF/DCTB): *m/z*: 1166.5 $[M]^+$. HRMS (MALDI-DCTB): *m/z* calcd for $C_{82}H_{58}N_2O_6$ $[M]^+$: 1166.4295, found: 1166.4225. UV-vis ($CHCl_3$): λ_{max} = 243 (ε = 46585 L.mol^{-1}.cm^{-1}). PL ($CHCl_3$): λ_{Em} = 348, 362 nm. M.p. = 136 °C.

{12-hydroxy-3,6,9-trimethoxy-6,9-diphenyl-14-[tris(propan-2-yl)silyl]tetradeca-1,4,7,10,13-pentayn-1-yl}tris(propan-2-yl)silane 11. To a solution of tri(isopropyl)silylacetylene (1.70 mL, 7.58 mmol) in dry THF (50 mL) under stirring at – 78 °C was added *n*-BuLi (2.90 mL, 7.25 mmol). The resulting solution was stirred 20 min. at – 78 °C and then 20 min. at room temperature. After cooling again at – 78 °C, a solution of the dialdehyde **10** (1.13 g, 3.05 mmol) in dry THF (25 mL) was added. The mixture was allowed to slowly warm up to room temperature and the stirring was maintained overnight. After treatment with saturated aqueous NH_4Cl, the aqueous layer was extracted with diethylether, and then the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (acetone/pentane 1:9) to give **11** as yellow oil in 82 % yield.

^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 42 H, Si-C*H*-CH_3), 2.83 (bs, 2 H, O*H*), 3.54-3.56 (m, 6 H, OCH_3), 5.21-5.25 (m, 2 H, C*H*OH), 7.36-7.48 (m, 6 H, *m*-, *p*-C_6H_5), 7.75-7.77 (m, 4 H, *o*-C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.0 (Si-*C*H-CH$_3$), 18.4 (Si-CH-CH_3), 52.4 (*C*H-OH), 53.3 (O-CH_3), 71.7 (*C*-OCH_3), 80.85, 80.88, 80.89, 84.2, 84.50, 84.51, 84.6, 86.37, 86.40 (C-*C*≡*C*-C and C-C≡*C*-Si), 103.3 (*C*≡C-Si), 126.4, 128.3 (*o*-, *m*-C_6H_5), 128.8 (*p*-C_6H_5), 139.5 (*i*-C_6H_5). MS (MALDI-TOF/ DCTB): *m/z*: 757.4 $[M+Na]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{46}H_{62}O_4NaSi_2$ $[M+Na]^+$: 757.4084, found: 757.4080.

{6,9-dimethoxy-3,12-dioxo-6,9-diphenyl-14-[tris(propan-2-yl)silyl]tetradeca-1,4,7,10,13-pentayn-1-yl}tris(propan-2-yl)silane 12. To a solution of the diol **11** (0.255 g, 0.347 mmol) in dry DCM (60 mL) at room temperature, was added MnO_2 (0.278 g, 3.20 mmol). The resulting mixture was stirred for 3 h at room temperature, and then filtered through celite. The filtrate was evaporated to dryness to give the diketone **12** as a pale brown solid in quantitative yield.

^{1}H NMR ($CDCl_3$): δ = 1.12-1.23 (m, 42 H, Si-C*H*-C*H*$_3$), 3.61 (s, 6 H, OC*H*$_3$), 7.41 (bs, 6 H, *m*-, *p*-C_6H_5), 7.73 (bs, 4 H, *o*-C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 10.9 (Si-*C*H-CH_3), 18.4 (Si-CH-*C*H$_3$), 53.8 (O*C*H$_3$), 71.9 (*C*-OCH_3), 83.96, 84.02, 85.5 (≡*C*-C-*C*≡), 87.1 (≡*C*-C=O), 99.4 (C≡*C*-Si), 104.6 (*C*≡C-Si), 126.2(7), 126.2(9), 128.7 (*o*-, *m*-*C*$_6$H$_5$), 129.4 (*p*-*C*$_6$H$_5$), 138.1(0), 138.1(3) (*i*-*C*$_6$H$_5$), 159.2 (*C*=O). MS (DCI/CH_4): *m/z*: 731.4 [MH]$^+$. HRMS (DCI/CH_4): *m/z* calcd for $C_{46}H_{59}O_4Si_2$ [MH]$^+$: 731.3952, found: 731.3965.

1-(4-{3,12-dihydroxy-12-[4-(1H-indol-1-yl)phenyl]-6,9-dimethoxy-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-1,4,7,10,13-pentayn-3-yl}phenyl)-1H-indole 15. To a solution of 1-(4-bromophenyl)-1H-indole (130 mg, 0.48 mmol) in THF (10 mL) was added *n*-BuLi (168 µL, 0.41 mmol) at -78°C. The reaction mixture was stirred during 1 h at -78 °C before adding a solution of the diketone **12** (125 mg, 0.17 mmol) in THF (3mL). The temperature was allowed to increase slowly up to -10 °C in 3h, then saturated aqueous NH_4Cl was added. The aqueous layer was extracted with ether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:Pentane 1:9) to give **15** as a light yellow solid in 85 % yield (162 mg). R_f (EtOAc:Heptane 5:5) = 0.45.

^{1}H NMR($CDCl_3$): δ = 1.12-1.23 (m, 42 H, Si-C*H*-C*H*$_3$), 3.16 (s, 2 H, OH), 3.65 (m, 6 H, OC*H*$_3$), 6.74 (d, $^3J_{HH}$ = 3.2 Hz, 2 H, H_3-indole), 7,22-7,30 (m, 4 H, H_6-, H_8-indole), 7.36-7.45 (m, 8 H, *p*-C_6H_5, *o*-C_6H_4-N, H_2-indole), 7.54 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, *m*-C_6H_5), 7.62 (m, 2 H, H_7-indole), 7.75 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, H_9-indole), 7.81-7.91 (m, 4 H, *m*-C_6H_4-N), 8.01 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, *o*-C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.23 (Si-*C*H-CH_3), 18.7 (Si-CH-CH_3), 53.6 (CH_3O), 65.1 (*C*-OH), 72.1 (*C*-OCH_3), 82.3, 84.6, 87.5, 88.1 (C-*C*≡*C*-C and C≡*C*-Si), 104.0 (C_3-indole), 106.0 (*C*≡C-Si), 110.6 (C_6-indole), 120.6 (*o*-*C*$_6$H$_4$-N), 121.3 (C_2-indole), 122.6 (C_9-indole), 124.0 (C_7-, C_8-indole), 126.7 (*o*-*C*$_6$H$_5$), 127.5 (*p*-*C*$_6$H$_5$), 127.8 (*m*-*C*$_6$H$_4$-N), 128.6 (*m*-*C*$_6$H$_5$), 129.1, 129.5 (C_4-, C_5-indole), 137.8 (*i*-*C*$_6$H$_4$-N), 139.6 (*i*-*C*$_6$H$_5$), 140.2 (*p*-C_6H$_4$-N). MS (MALDI-TOF/DCTB): *m/z*: 1116.6 $[M]^+$. HRMS (MALDI-DCTB): *m/z* calcd for $C_{74}H_{80}N_2O_4Si_2$ $[M]^+$: 1116.5657, found: 1116.5739. UV-vis ($CHCl_3$): λ_{max} = 267 (ε = 17860 L.mol^{-1}.cm^{-1}). PL ($CHCl_3$): λ_{Em} = 330, 480 nm. M.p. = 56 ˚C.

9-(4-{12-[4-(9H-carbazol-9-yl)phenyl]-3,12-dihydroxy-6,9-dimethoxy-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-1,4,7,10,13-pentayn-3-yl}phenyl)-9H-carbazole 16. To a solution of 9-(4-bromophenyl)-9H-carbazole (186 mg, 0.58 mmol) in THF (31 mL) under stirring at -78 ˚C was added *n*-BuLi (0.20 mL, 0.50 mmol). The reaction mixture was stirred during 1 hour at -78 ˚C before addition of a solution of the diketone **12** (151 mg, 0.21 mmol) in THF (3mL). The temperature was allowed to increase slowly up to -10 ˚C over 4 h. before addition of saturated aqueous NH_4Cl. The aqueous layer was extracted with diethylether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (Et_2O:Pentane 15:85) to give **16** as a yellow oil in 82 % yield (205 mg).

^{1}H NMR ($CDCl_3$): δ = 1.09-1.14 (m, 42 H, Si-C*H*-C*H*$_3$), 3.15 (bs, 2 H, OH), 3.57-3.65 (m, 6 H, OC*H*$_3$), 7,29-7,41 (m, 18 H, *m*-, *p*-C_6H_5, *o*-C_6H_4-N, H_6-, H_9-, H_{10}-, H_{13}-carbazole), 7.57-7.59 (m, 4 H, H_7-, H_{11}-carbazole), 7.79-7.86 (m, 4 H, *o*-C_6H_5), 8.03-8.05 (m, 4 H, *m*-C_6H_4-N), 8.14-8.19 (m, 4 H, H_8-, H_{12}-carbazole). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.1 (Si-*C*H-CH$_3$), 18.6 (Si-CH-*C*H$_3$), 53.5 (O*C*H$_3$), 65.0 (*C*-OH), 72.0 (*C*-OMe), 82.2(6), 82.3(2), 84.4(5), 84.5(0), 84.5(4), 87.2, 87.3, 88.3 (C-*C*≡*C*-C and C≡*C*-Si), 105.8, 105.9 (*C*≡C-Si), 109.7 (C_6-, C_{10}-carbazole), 120.1 (*o*-C_6H$_4$-N), 120.3 (C_8-, C_{12}-carbazole), 123.4 (C_3-, C_4-carbazole), 125.9 (C_9-, C_{13}-carbazole), 126.6 (*o*-C_6H$_5$), 126.9 (C_7-, C_{11}-carbazole), 127.6 (*m*-C_6H$_4$-N), 128.5 (*m*-C_6H$_5$), 129.0(7) (*p*-C_6H$_5$), 138.1(4) (C_2-, C_5-carbazole), 139.4, 140.1, 140.7 (*i*-C_6H$_5$, *i*-, *p*-C_6H$_4$-N). MS (MALDI-TOF/DCTB): *m/z* : 1216.6 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{82}H_{84}N_2O_4Si_2$: 1216.5970, found: 1216.6039. UV-vis ($CHCl_3$): λ_{max} = 242 nm (ε = 62445 L. mol^{-1}.cm^{-1}), 294 (37519). PL ($CHCl_3$): λ_{Em} = 347, 362 nm.

4-{12-[4-aminophenyl]-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-3,4,5,9,10, 11-hexaen-1,7,13-triyn-3-yl}-aniline 17. A solution of *p*-bromo-N,N-bis(trimethylsilyl)-aniline (0.40 mL, 1.42 mmol) in THF (1 mL) was added slowly at room temperature to a suspension of magnesium (33 mg, 1.36 mmol) in THF (0.5 mL). After the organo-magnesium derivative was formed, the resulting mixture was added to a solution of the diketone **12** (170 mg, 0.23 mmol) in THF (5 mL) at 0 °C. The stirring was maintained at 0 °C for 2 hours, and then overnight at room temperature. After treatment with water, the aqueous layer was extracted with diethylether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The obtained poorly stable pentaynediol **13** was directly used in the reduction step without further purification. The mixture was thus dissolved in DCM (70 mL), before addition of $SnCl_2$ (440 mg, 2.33 mmol) and then $HCl.Et_2O$ (2.31 mL, 4.62 mmol) at – 78 °C. The temperature was allowed to increase slowly up to – 20 °C, thus giving a red-dark mixture. Then aqueous 1 M NaOH (4.8 mL) was added and the mixture was allowed to warm up to room temperature while turning to dark-blue. After treatment with brine, the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (DCM/pentane 1:9 then 2:8) to give **17** as a green-gold solid in 53 % yield.

^{1}H NMR (THF D_8): δ = 1.20-1.29 (m, 42 H, Si-C*H*-C*H*$_3$), 5.30 (bs, 4 H, N*H*$_2$), 6.60-6.65 (m, 4 H, *m*-C_6*H*$_4$-N), 7.27-7.47 (m, 6 H, *m*-, *p*-C_6H_5), 7.63-7.68 (m, 4 H, *o*-C_6*H*$_4$-N), 7.83-7.93 (m, 4 H, *o*-C_6*H*$_5$). ^{13}C{^{1}H} NMR (THF D_8): δ = 12.4 (Si-*C*H-CH$_3$), 19.2 (Si-CH-*C*H$_3$), 99.9, 100.3, 100.4, 100.5, 100.7, 100.8, 101.5, 101.6, 106.1, 106.2, 106.3, 106.6, 106.9 (*C*≡*C*-Si and *C*-*C*≡*C*-*C*), 114.8, 114.9, 115.0 (*m*-*C*$_6$H$_4$-N), 126.1(6), 126.2(3), 126.9, 127.4, 127.5, 127.8, 128.7, 128.8, 129.2(8), 129.3(4), 129.4, 129.5, 129.6, 129.8, 129.9, 130.1 (*o*-, *m*-, *p*-*C*$_6$H$_5$ and *o*-*C*$_6$H$_4$-N), 137.6, 137.8, 138.5 (*i*-*C*$_6$H$_5$), 141.6, 141.7(6), 141.8(4) (*i*-*C*$_6$H$_4$-N), 144.2, 144.3, 144.7 (C=*C*=*C*=C), 151.5, 151.6(5), 151.6(8) (*p*-*C*$_6$H$_4$-N). MS (MALDI-TOF/DCTB): *m/z*: 820.4 [M]$^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{56}H_{64}N_2Si_2$: 820.4625, found: 820.4608. UV-vis ($CHCl_3$): λ_{max} = 622 nm (ε = 38654 L. mol^{-1}.cm^{-1}), 456 (25009), 379 (20804). M.p.(dec.) = 210 °C.

4-{12-[4-(dimethylamino)phenyl]-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-3,4,5,9,10,11-hexaen-1,7,13-triyn-3-yl}-N,N-dimethylaniline 18. A solution of *p*-bromo-N,N-dimethylaniline (327 mg, 1.63 mmol) in THF (1 mL) was added slowly at room temperature to a suspension of magnesium (39 mg, 1.60 mmol) in THF (0.5 mL). After the organo-magnesium derivative was formed, the resulting mixture was added to a solution of the diketone **12** (199 mg, 0.27 mmol) in THF (5 mL) at 0 °C. The stirring was maintained 2 hours at 0 °C, and then overnight at room temperature. After treatment with H_2O, the aqueous layer was extracted with diethylether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The obtained poorly stable pentaynediol **14** was directly used in the reduction step without further purification. The mixture was thus dissolved in Et_2O (70 mL), before adding $SnCl_2$ (520 mg, 2.75 mmol) and then $HCl.Et_2O$ (2.72 mL, 5.44 mmol) at – 78 °C. The temperature was allowed to increase slowly up to 15 °C, thus giving an intense red mixture. Then aqueous 1 M NaOH (5.8 mL) was added and the mixture was allowed to warm up to room temperature. After treatment with brine, the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (DCM/pentane 1:9 then 2:8) to give **18** as a dark-red solid in 29 % yield. ^{1}H NMR (THF D_8): δ = 1.18-1.28 (m, 42 H, Si-C*H*-C*H*$_3$), 2.97-3.05 (m, 12 H, N-C*H*$_3$), 6.68-6.81 (m, 4 H, *m*-C_6*H*$_4$-N), 7.26-7.49 (m, 6 H, *m*-, *p*-C_6H_5), 7.76-7.94 (m, 8 H, *o*-C_6*H*$_4$-N, *o*-C_6*H*$_5$). ^{13}C{^{1}H} NMR (THF D_8): δ = 12.4 (Si-*C*H-CH$_3$), 19.2 (Si-CH-*C*H$_3$), 40.1, 40.2 (N-*C*H$_3$), 100.5, 100.8, 101.6, 106.1, 106.1(7), 106.2(3) (*C*≡*C*-Si and *C*-*C*≡*C*-*C*), 112.8, 112.9, 113.1 (*m*-*C*$_6$H$_4$-N), 126.0, 126.1, 127.4, 127.5, 127.8, 128.7(5), 128.8(3), 129.3, 129.4, 129.5, 129.8 (*o*-, *m*-, *p*-*C*$_6$H$_5$ and *o*-*C*$_6$H$_4$-N), 137.6, 137.8, 138.6 (*i*-*C*$_6$H$_5$), 141.6 (*i*-*C*$_6$H$_4$-N), 144.2 (C=*C*=*C*=C), 151.9, 152.0, 152.1 (*p*-*C*$_6$H$_4$-N). MS (MALDI-TOF/DCTB): *m/z*: 876.5 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{60}H_{72}N_2Si_2$: 876.5234, found: 876.5291. UV-vis ($CHCl_3$): λ_{max} = 669 nm (ε = 66702 L. mol^{-1}.cm^{-1}), 510 (37959), 405 (31836). M.p.(dec.) = 222 °C.

1-(4-{12-[4-(1H-indol-1-yl)phenyl]-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-3,4,5,9,10,11-hexaen-1,7,13-triyn-3-yl}phenyl)-1H-indole 19. To a solution of the diol **15** (32 mg, 0.029 mmol) in dry dichloromethane (5 mL) at -78°C were added $SnCl_2$ (55 mg, 0.29 mmol) and then $HCl.Et_2O$ (0.29 mL, 0.58 mmol). The reaction mixture was then immediately removed from the cold bath and stirred at room temperature during 10 min. before adding aqueous 1M NaOH (0.7 mL, 0.7 mmol). The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc:Pentane 2:98) to give **19** as a blue-violet solid in 74 % yield (22 mg). R_f (EtOAc:Heptane 5:95) = 0.35. ^{1}H NMR ($CDCl_3$): δ = 1.14-1.27 (m, 42 H, Si-C*H*-C*H*$_3$), 6.64-6.79 (m, 2 H, *H*$_3$-indole), 7.18-7.25 (m, 4 H, *H*$_6$-, *H*$_8$-indole), 7.38-7.76 (m, 16 H, *o*-C_6*H*$_4$-N, *m*-, *p*-C_6*H*$_5$, *H*$_2$-, *H*$_7$-, *H*$_9$-indole), 7.94-8.08 (m, 8 H, *m*-C_6*H*$_4$-N, *o*-C_6*H*$_5$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.5 (Si-*C*H-CH$_3$), 18.8 (Si-CH-*C*H$_3$), 99.2, 99.9, 103.9, 104.2, 104.2(6), 104.3(3), 104.4(6), 104.5(0), 104.6 (-*C*≡*C*-, -*C*≡*C*-Si, *C*$_3$-indole), 110.7 (*C*$_6$-indole), 120.7, 120.8, 121.2, 121.3, 122.7, 123.8, 124.0 (*o*-*C*$_6$H$_4$-N, *C*$_2$-, *C*$_7$-, *C*$_8$-, *C*$_9$-indole), 127.3, 127.4, 127.5, 127.6 (*o*-, *p*-*C*$_6$H$_5$), 128.5, 128.7, 128.7(7), 128.8(1), 128.8(7), 128.8(9) (*m*-*C*$_6$H$_5$, *o*-, *m*-*C*$_6$H$_4$-N), 129.2, 129.6

(C_4-, C_5-indole), 131.0, 134.5, 134.6, 135.5, 135.6, 136.1, 137.0 (*i*-C_6H_4-N, *i*-C_6H_5), 140.2 (*p*-C_6H_4-N), 146.2, 146.4 (C=*C*=*C*=C). MS (MALDI-TOF/DCTB): *m/z*: 1020.5 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{72}H_{72}N_2Si_2$ $[M]^+$: 1020.5193, found: 1020.5234. UV-vis ($CHCl_3$): λ_{max} = 599 (ε = 182037 $L.mol^{-1}.cm^{-1}$), 432, 268 nm. PL ($CHCl_3$): λ_{Em} = 499 nm. M.p. = 168 °C.

9-(4-{12-[4-(9H-carbazol-9-yl)phenyl]-6,9-diphenyl-1,14-bis[tris(propan-2-yl)silyl]tetradeca-3,4,5,9,10,11-hexaen-1,7,13-triyn-3-yl}phenyl)-9H-carbazole 20. To a solution of the pentaynediol **16** (72 mg, 0.06 mmol) in dry diethylether (40 mL) at -78 °C were added $SnCl_2$ (112 mg, 0.59 mmol) and then $HCl.Et_2O$ (0.60 mL, 0.12 mmol). The temperature of the reaction mixture was slowly increased up to -10 °C, thus giving a purple-blue mixture. Then aqueous 1M NaOH (1.7 mL, 0.17 mmol) was added and the mixture was allowed to warm up to room temperature. After treatment with brine, the aqueous layer was extracted with DCM and the combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (DCM:pentane 2:98 then 1:9) to give **20** as a purple-blue solid in 52 % yield.

^{1}H NMR ($CDCl_3$): δ = 1.18-1.26 (m, 42 H, Si-C*H*-C*H*$_3$), 7.29-7.67 (m, 22 H, *m*-, *p*-C_6H_5, *o*-C_6H_4-N, H_6-, H_7-, H_9-, H_{10}-, H_{11}-, H_{13}-carbazole), 7.94-7.96 (m, 4 H, *o*-C_6H_5), 8.08-8.17 (m, 8 H, H_8-, *m*-C_6H_4-N, H_{12}-carbazole). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.4 (Si-*C*H-CH$_3$), 18.8 (Si-CH-*C*H$_3$), 103.9, 104.0(5), 104.1(3), 104.2, 104.3, 104.4(6), 104.5(0), 104.6(1), 104.6(3), 104.6(5), 104.6(8), 104.9, 105.0 (*C*≡*C*-Si and *C*-*C*≡*C*-*C*), 109.8(5), 109.9(1) (C_6-, C_{10}-carbazole), 120.3, 120.3(6) (C_8-, C_{12}-carbazole), 123.4(3) (C_3-, C_4-carbazole), 126.0, 126.1, 126.7(4), 126.6(8), 126.9, 127.2, 127.3, 127.5, 128.6, 128.7, 128.8, 128.9, 129.1, 129.2, 129.3, 129.7, 130.0 (*o*-, *m*-, *p*-C_6H_5, *o*-, *m*-C_6H_4-N, C_7-, C_9-, C_{11}-, C_{13}-carbazole), 135.3, 136.0, 138.3, 140.4, 140.5 (*i*-C_6H_5, *i*-, *p*-C_6H_4-N, C_2-, C_5-carbazole), 146.4, 146.6 (C=*C*=*C*=C). MS (MALDI-TOF/DCTB): *m/z*: 1120.55 $[M]^+$. HRMS (MALDI-TOF/DCTB): *m/z* calcd for $C_{80}H_{76}N_2Si_2$: 1120.5547, found: 1120.5620. UV-vis ($CHCl_3$): λ_{max} = 597 (ε = 66562 $L.\ mol^{-1}.cm^{-1}$), 243 nm. PL ($CHCl_3$): λ_{Em} = 501 nm. M.p. = 190 °C.

Crystallographic details

Intensity data were collected at a temperature of 193(2)K on a Bruker-AXS APEX II diffractometer using a 30 W air-cooled microfocus source (ImS) with focusing multilayer optics, with graphite-monochromated MoKα radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied (S^1) (S^2). The structures were solved by direct methods, using SHELXS-97 (S^3) and refined using the least–squares method on F^2(Si^4). All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model.

Selected crystal data

6 (CCDC 886379): $C_{54.50}H_{33}ClN_2$, M= 751.28, Orthorhombic, space group $P\ \bar{1}$, a =12.456(4) Å, b = 16.127(5) Å, c = 20.503(7) Å, V = 4118(2) Å^3, Z = 4, crystal size 0.60 x 0.10 x 0.05 mm^3, 76028 reflections collected (6723 independent, R_{int} = 0.3206), 566 parameters, 139 restraints, $R1[I>2\sigma(I)]$ = 0.0792, $wR2$ [all data] = 0.2387, largest diff. peak and hole: 0.161 and -0.152 e.Å^{-3}. Molecular view: see Fig. 2.

17 (CCDC 886380): $C_{56}H_{64}N_2Si_2$, M= 821.27, Triclinic, space group $P\ \bar{1}$, a =7.4967(6) Å, b = 7.7637(7) Å, c = 21.2257(17) Å, α = 97.551(4)°, β = 93.735(4)°, γ = 96.544(4)°, V = 1212.66(18) Å^3, Z = 1, crystal size 0.34 x 0.20 x 0.02 mm^3, 24394 reflections collected (4837 independent, R_{int} = 0.0348), 285 parameters, $R1[I>2\sigma(I)]$ = 0.0476, $wR2$ [all data] = 0.1257, largest diff. peak and hole: 0.292 and -0.223 e.Å^{-3}. Molecular view: see Fig. 2.

18 (CCDC 886381): $C_{60}H_{72}N_2Si_2$, M= 877.38, Triclinic, space group $P\ \bar{1}$, a = 9.2348(9) Å, b = 9.3293(9) Å, c = 15.6051(16) Å, α = 104.252(5)°, β = 91.728(4)°, γ = 95.653(4)°, V = 1294.7(2) Å^3, Z = 1, crystal size 0.20 x 0.10 x 0.05 mm^3, 35105 reflections collected (5230 independent, R_{int} = 0.0418), 297 parameters, $R1[I>2\sigma(I)]$= 0.0448, $wR2$ [all data] = 0.1214, largest diff. peak and hole: 0.352 and -0.297 e.Å^{-3}. Molecular view: see Fig. S1.

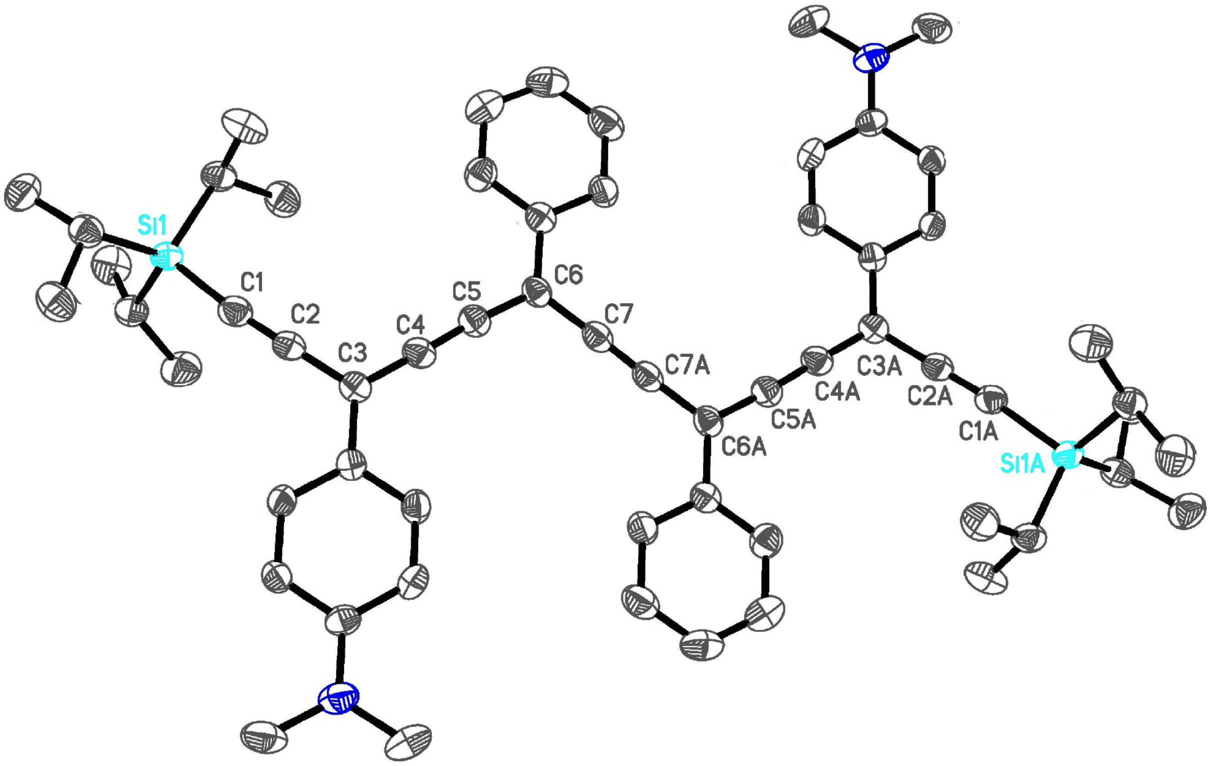

Fig. S1. Molecular view of the *carbo*-DAPB **18** (Scheme 2).

References:

[S1] SAINT-*NT*; Bruker AXS Inc.: Madison, Wisconsin, 2000.

[S2] SADABS, Program for data correction, Bruker−AXS.

[S3] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

[S4] SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr.,* Sect. A **2008**, 64, 112–122.