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Supporting Information

Synthesis of Compounds Presenting Three and Four Anthracene Units as Potential Connectors to Mediate Infinite Lateral Growth at the Air/Water Interface

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Synthesis of Compounds Presenting Three and Four Anthracene Uunits as Potential Connectors to Mediate Infinite Lateral Growth at the Air/Water Interface

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Compound 3. 9-anthracene carboxylic acid **1** (2.75 g, 12.37 mmol) and 3-amino-2,2-bis(aminomethyl)propan-1-ol trihydrochloride **2** (1.00 g, 4.1 mmol) were dissolved in a mixture of dry CH_2Cl_2 (120 mL), dry DMF (40 mL), and diisopropylethylamine (7.75 g, 60 mmol). The reaction mixture was cooled to 0°C before PyBop (6.76 g, 13 mmol) was added. The cooling bath was removed and the mixture was stirred overnight at room temperature. The solution was diluted with CH_2Cl_2 (300 mL), washed twice with 1 M HCl, and once with brine. The combined organic phases were dried over $MgSO_4$ and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (1:1 hexane/EtOAc) affording 1.51 g (49%) of the product as a yellowish solid. R_f = 0.46 (1:1 hexane/EtOAc); m.p. 248 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (d, 6 H, $^3J_{H,\,H}$ = 6.00 Hz, C*H*NH), 3.79 (d, 2 H, $^3J_{H,\,H}$ = 6.6 Hz, C*H*OH), 5.05 (t, 1 H, $^3J_{H,\,H}$ = 7.05 Hz, CHO*H*), 7.48 (t, 6 H, $^3J_{H,\,H}$ = 7.5 Hz, Ar*H*), 7.57 (t, 6 H, $^3J_{H,\,H}$ = 7.5 Hz, Ar*H*), 7.97 (d, 6 H, $^3J_{H,\,H}$ = 8.4 Hz, Ar*H*), 8.04 (d, 6 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 8.07 (br, 3 H, CHN*H*), 8.41 (s, 1 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.08, 46.96, 61.09, 124.61, 125.41, 126.95, 128.08, 128.79, 128.87, 130.67, 131.02, 171.76 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 745.2911 $[M + H]^+$, calcd monoisotopic peak ($^{12}C_{50}{}^1H_{39}{}^{14}N_3{}^{16}O_4$) 745.2941; elemental analysis calcd (%) for $C_{50}H_{39}N_3O_4$ (745.86): C 80.52, H 5.27, N 5.63; found C 80.67, H 5.29, N 5.66.

Compound 6a. **4** (2.3 g, 5.18 mmol) and acid **5** (934 mg, 5.18 mmol) were dissolved in a mixture of dry CH_2Cl_2 (20 ml), dry DMF (10 ml), and diisopropylethylamine (DIEA, 3.8 ml, 21.8 mmol). The reaction mixture was cooled to 0°C before PyBop (2.84 g, 5.45 mmol) was added. The cooling bath was removed and the mixture was stirred overnight. The solution was diluted with CH_2Cl_2, washed twice with 1 M HCl, and once with brine. The combined organic phases were dried over $MgSO_4$, filtered and concentrated to dryness. The crude product was purified by column chromatography (10:1 hexane/EtOAc then 3:1 hexane/EtOAc) and afforded 732 mg (52%) of product as colorless oil. R_f = 0.44 (3:1 hexane/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (s, 3 H, CH_3), 3.99 (s, 6H, CCH_2), 4.55 (s, 6H, OCH_2Ph), 6.57 (s, 1H, N*H*), 7.26 – 7.35 (m, 15H, Ar*H*), 7.75 (d, 2 H, $^3J_{H,\,H}$ = 8.4 Hz, Ar*H*), 8.04 (d, 2H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = δ = 52.35, 60.39, 69.01, 73.45, 126.97, 127.6, 127.66, 128.38, 129.75, 132.48, 138.19, 139.39, 166.37, 166.49 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 576.2351 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{34}{}^1H_{35}{}^{14}N^{16}O_6Na$) 576.2356; EA calcd (%) C: 73.76, H: 6.37, N: 2.53, found C: 73.88 H: 6.46 N: 2.57.

Compound 6b. Ester **6a** (530 mg, 0.957 mmol) was dissolved in a mixture of THF/ MeOH/ KOH (aqueous solution, 1M) (10 ml: 10 ml: 10 ml). Additionally, solid KOH (336 mg, 6 mmol) was added. The mixture was refluxed at 100°C for 12 h. The solvent was removed under reduced pressure. The residue was dissolved in water. Precipitation was achieved by adding concentrated HCl (37 %). The solid was separated and dissolved in acetone. The solution was dried over $MgSO_4$ and the solvent removed *in vacuo*. 494 mg (96 %) of **6b** as colourless solid were obtained. R_f = 0.27 (1:20 MeOH/DCM); mp 187 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.35 (br, 1H, COO*H*), 3.88 (s, 6H, CCH_2), 4.38 (s, 6H, OCH_2Ph), 6.74 (s, 1H, N*H*), 7.14 (br, 15H, Ar*H*), 7.43 (d, 2H, $^3J_{H,\,H}$ = 8.1 Hz Ar*H*), 7.74 (d, 2H, $^3J_{H,\,H}$ = 8.1 Hz Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 60.46, 68.89 , 73.25, 126.54, 127.51, 128.27, 129.12, 136.54, 138.17, 140.45, 167.97,

172.74 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 576.2198 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{33}{}^{1}H_{33}{}^{14}N^{16}O_6Na$) 562.2200; EA calcd (%) C: 70.45, H: 5.91, N: 2.49, found C: 70.57 H: 6.01 N: 2.57.

Compound 8. In a thoroughly dried flask, NaH (190 mg, 60% dispersion in mineral oil, 8 mmol) was mixed with THF (15 mL) in an inert atmosphere, and degassed in three freeze-pump-thaw cycles. 2,5,8,11,15,18,21,24-Octaoxapentacosan-13-ol (0.77 g, 2 mmol) was added, forming a slight yellow suspension, and the mixture was let stirred for 15 min before 4-(bromomethyl)benzoic acid (0.48 g, 2.2 mmol) was added. The whole mixture was let stirring overnight. The reaction was worked up by concentrating and filtered through a short plug of silica gel by washing with MeOH/DCM (1:10). The combined filtrate was further purified by column chromatography (silica gel, 1:30 MeOH/DCM to 1:10 MeOH/DCM). 0.77 g (74%) of pure product was obtained as a colorless liquid.^{1}H NMR (300 MHz, MeOD): δ = 3.35 (s, 6H, OCH_3), 3.53 (m, 4H, (CH_2)$_2$CH), 3.67-3.61 (m, 24H, CH_2), 3.78 (m, 1H, C*H*), 4.79 (s, 2H, CH_2Ph), 7.52 (m, 2H, Ar*H*), 8.02 (m, 2H, Ar*H*) ppm, ^{13}C NMR (75 MHz, MeOD): δ = 60.0, 72.1, 72.3, 72.6, 73.1, 73.2, 73.7, 79.7, 129.3, 131.6, 132.1, 146.4, 170.7 ppm, MS (EI): *m/z* = 518.2727 $[M]^+$ calcd for $C_{25}H_{42}O_{11}$: 518.2723, elemental analysis calcd (%) for $C_{25}H_{42}O_{11}$ (518.59): C 57.90, H 8.16; found C 58.01, H 8.28.

Compound 9b. Ester **9a** (700 mg, 1.124 mmol) was dissolved in a mixture of THF (8 mL), MeOH (8 mL), and 1M aqueous KOH (8 mL). Then solid KOH (756 mg, 13.5 mmol) was added. The mixture was refluxed at 100°C for 12 hrs. The solvent was removed under reduced pressure and the solid residue was dissolved in 40 mL of water. Addition of 5 mL of concentrated HCl to the solution caused precipitation of yellowish solid. The solid was filtered and then dissolved in acetone. The solution was dried over $MgSO_4$ and the solvent removed under reduced pressure affording 664 mg (97 %) of **9b** as yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.33 (s, 9 H, OCH_3), 3.58 – 3.85 (m, 30 H, OCH_2), 4.14 – 4.23 (m, 6 H, OCH_2), 7.29 (s, 2 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.00, 68.90, 69.70, 70.30, 70.50, 70.70, 70.80, 71.90, 126.54, 127.51, 128.27, 109.60, 124.20, 143.21, 152.32, 170.43 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 631.2944 $[M + Na]^+$, calcd monoisotopic peak ($^{12}C_{28}{}^{1}H_{48}{}^{16}O_{14}Na$) 631.2942, elemental analysis calcd (%) for $C_{28}H_{48}O_{14}$ (608.67): C 55.25, H 7.95; found C 55.43, H 8.04.

Compound 10. The preparation of the compound was carried out according to the general procedure for esterification. **3** (250 mg, 0.335 mmol), DPTS (116.7 mg, 0.4025 mmol), acid **7** (59.7 mg, 0.335 mmol), dry CH_2Cl_2 (15 mL), dry DMF (5 mL), EDC (77.16 mg, 0.4025 mmol) were used in the reaction. The crude product was purified by column chromatography on silica gel (1:1 hexane/EtOAc then 1:1 hexane/EtOAc then EtOAc) affording yellow solid. Yield 89.5 mg (29%); R_f = 0.3 (CH_2Cl_2/MeOH 100:1); m.p. 194 – 196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.07 (s, 3 H, CH_3), 3.26 (m, 3 H), 3.38 (m, 6 H), 3.54 (m, 3 H), 3.95 (d, 6 H, $^3J_{H,\ H}$ = 6.3 Hz, CH_2NH), 4.24 (s, 2 H, COOCH_2O), 4.51 (s, 2 H, CCH_2O), 7.45 – 7.61 (m, 12 H, Ar*H*), 7.99 (d, 6 H, $^3J_{H,\ H}$ = 8.4 Hz, Ar*H*), 8.11 (d, 6 H, $^3J_{H,\ H}$ = 8.7 Hz, Ar*H*), 8.15 (br, 3 H, N*H*) ppm; ^{13}C NMR (75

MHz, $CDCl_3$): δ = 24.93, 25.62, 58.59, 63.88, 68.9, 70.05, 70.58, 70.87, 71.60, 124.65, 125.49, 127.0, 128.13, 128.75, 131.02, 131.13, 170.9, 171.34 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 906.3766 [*M* + H]$^+$, elemental analysis calcd (%) for $C_{57}H_{51}N_3O_8$ (906.03): C 75.56, H 5.67, N 4.64; found C 75.68, H 5.75, N 4.66.

Compound 11. The preparation of the compound was carried out according to the general procedure for esterification. **3** (150 mg, 0.2 mmol), DPTS (59.1 mg, 0.2 mmol), acid **8** (69 mg, 0.134 mmol), dry CH_2Cl_2 (4 mL), dry DMF (1 mL), EDC (38.2 mg, 0.2 mmol) were used in the reaction. The crude product was subjected to preparative GPC yielding 89 mg (53%) of **11** as colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (s, 6 H, C*H*$_2$NH), 4.01 (s, 6 H, C*H*$_2$O), 4.53 (s, 6 H, OC*H*$_2$Ph), 4.75 (s, 2 H, CC*H*$_2$), 6.23 (s, 1 H, N*H*), 7.25 - 7.31 (m, 15 H, Ar*H*), 7.47 - 7.6 (m, 12 H, Ar*H*), 7.69 (d, 2 H, $^3J_{H,\,H}$ = 8.4 Hz, Ar*H*), 8.01 (br, 3 H, CON*H*), 8.04 (d, 6 H, $^3J_{H,\,H}$ = 8.1 Hz, Ar*H*), 8.15 (d, 6 H, $^3J_{H,\,H}$ = 6.9 Hz, Ar*H*), 8.25 (d, 2 H, $^3J_{H,\,H}$ = 8.1 Hz, Ar*H*), 8.52 (s, 3 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.70, 39.73, 58.95, 59.03, 70.46, 70.54, 70.59, 70.90, 71.32, 71.58, 71.87, 71.94, 78.39, 78.74, 96.12, 124.58, 125.47, 127.01, 127.39, 127.74, 128.17, 128.78, 128.84, 130.00, 130.26, 130.76, 171.26 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1246.567 [*M* + H]$^+$, calcd monoisotopic peak ($^{12}C_{75}{}^1H_{80}{}^{14}N_3{}^{16}O_{14}$) 1246.564, elemental analysis calcd (%) for $C_{75}H_{79}N_3O_{14}$ (1246.44): C 72.27, H 6.39, N 3.37; found C 72.41, H 6.44, N 3.40.

Compound 12. The preparation of the compound was carried out according to the general procedure for esterification. **3** (150 mg, 0.2 mmol), DPTS (59.1 mg, 0.2 mmol), acid **9b** (81.6 mg, 0.134 mmol), dry CH_2Cl_2 (4 mL), dry DMF (1 mL), EDC (38.2 mg, 0.2 mmol) were used in the reaction. The crude product was subjected to preparative GPC yielding 78.7 mg (44%) of **12** as colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.3 (s, 9 H, OC*H*$_3$), 3.36 (s, 6 H, C*H*$_2$NH), 3.81 – 3.36 (m, 24 H, OC*H*$_2$) 3.94 (d, 6 H, $^3J_{H,\,H}$ = 4.3 Hz, PhOCH$_2$C*H*$_2$), 4.23 (t, 6 H, $^3J_{H,\,H}$ = 4.3 Hz, PhOC*H*$_2$), 4.65 (s, 2 H, CC*H*$_2$), 7.47 - 7.6 (m, 18 H, Ar*H*), 7.62 (s, 2 H, Ar*H*), 8.04 (d, 6 H, $^3J_{H,\,H}$ = 8.1 Hz, Ar*H*, 3 H, N*H*), 8.15 (d, 2H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 8.52 (s, 3 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.57, 45.94, 58.98, 62.46, 68.84, 69.52, 70.39, 70.54, 70.68, 71.83, 71.92, 72.4, 109.4, 123.67, 124.61, 125.5, 127.0, 128.16, 128.8, 131.18, 143.11, 152.53, 167.28, 171.12 ppm; MS (MALDI-TOF, DCTB Mix 1:10): *m/z* = 1358.27 [*M* + Na]$^+$, calcd monoisotopic peak ($^{12}C_{78}{}^1H_{85}{}^{14}N_3{}^{16}O_{17}Na$) 1358.58, elemental analysis calcd (%) for $C_{78}H_{85}N_3O_{17}$ (1336.52): C 70.10, H 6.41, N 3.14; found C 70.24, H 6.48, N 3.20.

Compound 13a. **3** (609 mg, 0.817 mmol) and DPTS (240 mg, 0.817 mmol) were added to a solution of acid **6b** (300 mg, 0.56 mmol) in a mixture of dry CH_2Cl_2 (25 mL) and dry DMF (5 mL) at room temperature. After 15 min EDC (157 mg, 0.817 mmol) was added and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 and washed twice with brine. The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure. 227 mg (23%) of **13a** as yellowish solid were collected after the preparative GPC separation. M.p. 148 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (s, 6 H, C*H*$_2$NH), 4.01 (s, 6 H, C*H*$_2$O), 4.53 (s, 6 H, OC*H*$_2$Ph), 4.75 (s, 2 H, CC*H*$_2$), 6.23 (s, 1 H, N*H*), 7.25 - 7.31 (m, 15 H, Ar*H*), 7.47 -

7.6 (m, 12 H, Ar*H*), 7.69 (d, 2H, $^{3}J_{H,H}$ = 8.4 Hz, Ar*H*), 8.01 (br, 3 H, CON*H*), 8.04 (d, 6 H, $^{3}J_{H,H}$ = 8.1 Hz, Ar*H*), 8.15 (d, 6 H, $^{3}J_{H,H}$ = 6.9 Hz, Ar*H*), 8.25 (d, 2 H, $^{3}J_{H,H}$ = 8.1 Hz, Ar*H*), 8.52 (s, 3 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.84, 45.81, 60.43, 63.60, 69.94, 73.43, 122.21, 123.77, 124.65, 125.50, 127.07, 127.21, 127.59, 128.18, 128.39, 128.83, 128.94, 130.35, 130.86, 131.17, 131.33, 137.55, 138.15, 166.32, 171.31 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1289.502 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{83}{}^{1}H_{70}{}^{14}N_4{}^{16}O_9Na$) 1289.504, elemental analysis calcd (%) for $C_{83}H_{70}N_4O_9$ (1267.47): C 78.65, H 5.57, N 4.42; found C 78.73, H 5.61, N 4.45.

Compound 13b. The protected alcohol **13a** (43.5 mg, 0.034 mmol) was dissolved in EtOH (5 mL) and EtOAc (3 mL) and Pd/C (40 mg, 10% Pd loading) was added. The mixture was placed in a Parr tube and stirred at room temperature under a hydrogen pressure of 3 bar overnight. The solution was filtered through celite and the solvent was removed under reduced pressure. The crude reaction mixture was subjected to the preparative GPC yielding 9.6 mg (28 %) of **13b** as colourless oil. M.p. 148 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (s, 6 H, C*H*$_2$NH), 4.00 (s, 6 H, C*H*$_2$O), 4.75 (s, 2 H, CC*H*$_2$), 6.23 (s, 1 H, N*H*), 7.47 - 7.6 (m, 12 H, Ar*H*), 7.69 (d, 2H, $^{3}J_{H,H}$ = 8.4 Hz, Ar*H*), 8.01 (br, 3 H, CON*H*), 8.04 (d, 6 H, $^{3}J_{H,H}$ = 8.1 Hz, Ar*H*), 8.15 (d, 6 H, $^{3}J_{H,H}$ = 6.9 Hz, Ar*H*), 8.25 (d, 2 H, $^{3}J_{H,H}$ = 8.1 Hz, Ar*H*), 8.52 (s, 3 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.84, 45.81, 60.43, 63.60, 69.94, 122.21, 123.77, 124.65, 125.50, 127.07, 127.21, 128.18, 128.39, 128.94, 130.35, 130.86, 131.17, 131.33, 138.15, 166.32, 171.31 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1019.3638 $[M+Na]^+$, calcd monoisotopic peak ($^{12}C_{62}{}^{1}H_{52}{}^{14}N_4{}^{16}O_9Na$) 1019.3632.

Compound 15a. To a solution of **14a** (530 mg, 0.42 mmol) in dry MeOH (20 mL) anthracene-9-carbaldehyde (354 mg, 1.72 mmol) was added. The mixture was stirred at room temperature for 3 days. Then the solvent was removed *in vacuo*. Chromatographic purification (10:1 hexane/EtOAc/ 5% triethylamine then 1: 10 hexane/EtOAc/ 5% triethylamine) afforded 772 mg (92%) of **15a** as yellow oil. R_f = 0.35 ($CHCl_3$/acetone 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.39 (s, 12 H, C*H*$_3$), 3.53 (d, 4 H, $^{3}J_{H,H}$ = 13.8 Hz, ArC*H*$_2$Ar), 3.57 (t, 8H, $^{3}J_{H,H}$ = 2.55 Hz, C*H*$_2$), 3.67 – 3. 79 (m, 24H, OCH$_2$C*H*$_2$), 4.07 (t, 8 H, $^{3}J_{H,H}$ = 4.95 Hz, C*H*$_2$), 3.37 (t, 8 H, $^{3}J_{H,H}$ = 5.1 Hz, C*H*$_2$), 4.79 (d, 4 H, $^{3}J_{H,H}$ = 13.2 Hz, ArC*H*$_2$Ar), 7.06 – 7.2 (m, 18 H, Ar*H*), 7.69 (d, 8 H, $^{3}J_{H,H}$ = 8.1 Hz, Ar*H*), 8.05 (s, 4 H, Ar*H*), 8.44 (d, 8 H, $^{3}J_{H,H}$ = 8.7 Hz, Ar*H*), 9.36 (s, 4 H, C*H*NAr) ppm;^{13}C NMR (75 MHz, $CDCl_3$): 31.55, 59.04, 70.57, 70.69, 71.95, 73.45, 76.62, 120.97, 124.53, 124.76, 125.68, 125.86, 128.49, 130.02, 130.40, 130.67, 135.83, 148.07, 155.19, 158.60 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1997.957 $[M + H]^+$, calcd monoisotopic peak ($^{12}C_{124}{}^{1}H_{132}{}^{14}N_4{}^{16}O_{20}$) 1997.951, elemental analysis calcd (%) for $C_{124}H_{132}N_4O_{20}$ (1998.39): C 74.53, H 6.66, N 2.80; found C 74.73, H 6.75, N 2.88.

Compound 15b. Anthracene-9-carbaldehyde (3.52 g, 17.05 mmol) was added to a solution of **14b** (3.5 g, 4.27 mmol) in dry MeOH (350 mL). The mixture was stirred at reflux overnight. Size exclusion column chromatography afforded 6.05 g (90 %) of **15b** as orange solid. M.p. 277 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, 12 H, $^{3}J_{H,H}$ = 6.6 Hz, C*H*$_3$), 1.47 – 1.57 (m, 24 H, C*H*$_2$), 2.1 – 2.13 (m, 8 H, OCH$_2$), 3.49 (d, 4 H, $^{3}J_{H,H}$ = 12.9 Hz, ArC*H*$_2$Ar), 4.12 (t, 8 H, $^{3}J_{H,H}$ = 7.4 Hz, OC*H*$_2$), 4.74 (d, 4 H, $^{3}J_{H,H}$ = 12.9 Hz,

ArC*H*$_2$Ar), 7.05 – 7.2 (m, 16 H, Ar*H*), 7.7 (d, 8 H, $^3J_{H,\,H}$ = 8.1 Hz, Ar*H*), 8.06 (s, 4 H, Ar*H*), 8.7 (d, 8 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 9.38 (s, 4 H, C*H*N) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):14.17, 22.96, 26.13, 30.43, 31.63, 32.30, 75.72, 120.93, 124.60, 124.74, 125.84, 126.79, 130.39, 130.69, 135.90, 147.74, 155.53, 158.41 ppm; MS (MALDI-FT, 3-HPA) *m/z* = 1573.841 [*M* + Na]$^+$, calcd monoisotopic peak ($^{12}C_{112}{}^1H_{109}{}^{14}N_4{}^{16}O_4Na$) 1573.845, elemental analysis calcd (%) for $C_{112}H_{110}N_4O_4$ (1576.10): C 89.35, H 7.03, N 3.55; found C 89.46, H 7.12, N 3.61.

Compound 16a. Sodium borohydride (9.3 mg, 0.25 mmol) was added to a solution of **15a** (120 mg, 0.06 mmol) in MeOH (20 mL). The mixture was stirred at room temperature overnight. The excess of sodium borohydride was quenched by the slow addition of hydrochloric acid. The pH of the mixture was adjusted to 12 by addition of 1M NaOH and then extracted times with DCM (3 x 15 mL). The combined organic layers were washed with water, brine, and then dried over $MgSO_4$. The solvent was removed under reduced pressure. No further purification of **16a** was necessary. Yellow oil; yield 118 mg (98 %); R_f = 0.21 ($CHCl_3$/acetone 1:1); ^{1}H (300 MHz, $CDCl_3$): δ = 3.18 (d, $^3J_{H,\,H}$ = 10.2 Hz, 4 H, ArC*H*$_2$Ar), 3.39 (s, 12 H, CH_3) 3.59 – 3.56 (m, 40H, OC*H*$_2$), 3.68 – 3.76 (m, 8H, OCH_2CH_2), 4.02 (br, 8 H, OC*H*$_2$), 4.21 (br, 8 H, OC*H*$_2$), 4.6 (d, 4 H, $^3J_{H,\,H}$ = 14.2 Hz, ArC*H*$_2$Ar), 4.76 (br, 8 H, ArC*H*$_2$NH), 6.48 (s, 8 H, Ar*H*) , 6.92 (t, 8 H, $^3J_{H,\,H}$ = 7.6 Hz, Ar*H*), 7.13 (t, 8 H, $^3J_{H,\,H}$ = 7.5 Hz, Ar*H*), 7. 67 (d, 8 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 7.8 (d, 8 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 8.06 (s, 4 H, Ar*H*); ^{13}C (75 MHz, $CDCl_3$): δ = 31.6, 41.07, 59.04, 70.57, 70.69, 71.97, 73.16, 112.65, 113.20, 120.54, 120.94, 123.58, 124.56, 125.73, 126.66, 127.35, 128.67, 129.06, 129.31, 129.87, 130.33, 130.90, 131.36, 135.82, 143.45, 148.94 ppm; MS (MALDI-FT, DCTB mix): *m/z* = 2028.002 [*M* + Na]$^+$, calcd monoisotopic peak ($^{12}C_{124}{}^1H_{140}{}^{14}N_4{}^{16}O_{20}Na$) 2027.9959, calcd monoisotopic peak ($^{12}C_{112}{}^1H_{109}{}^{14}N_4{}^{16}O_4Na$) 1573.845, elemental analysis calcd (%) for $C_{124}H_{140}N_4O_{20}$ (2006.45): C 74.36, H 7.03, N 2.79; found C 74.36, H 7.11, N 2.87.

Compound 16b. $LiAlH_4$ (9.3 mg, 0.25 mmol) was added to a solution of **15b** (120 mg, 0.06 mmol) in THF (20 mL). The mixture was stirred at room temperature overnight. The excess of $LiAlH_4$ was quenched by the slow addition of water. Then 1M H_2SO_4 was added until the solution became homogeneous and the solution was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with water and brine and then dried over $MgSO_4$. The solvent was removed under reduced pressure. Purification of **16b** was carried out by means of preparative HPLC GPC. Yellow oil; yield 128 mg (79 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (br, 12 H, C*H*$_3$), 1.48 (br, 24 H, C*H*$_2$), 2.05 (br, 8 H, OCH_2), 3.23 (d, 4 H, $^3J_{H,\,H}$ = 14.2 Hz, ArC*H*$_2$Ar), 3.98 (t, 8 H, $^3J_{H,\,H}$ = 7.4 Hz, OC*H*$_2$), 4.6 (d, 4 H, $^3J_{H,\,H}$ = 14.2 Hz, ArC*H*$_2$Ar), 4.76 (br, 8 H, ArC*H*$_2$NH), 6.51 (s, 8 H, Ar*H*) , 6.92 (t, 8 H, $^3J_{H,\,H}$ = 7.6 Hz, Ar*H*), 7.13 (t, 8 H, $^3J_{H,\,H}$ = 7.5 Hz, Ar*H*), 7. 67 (d, 8 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 7.81 (d, 8 H, $^3J_{H,\,H}$ = 8.7 Hz, Ar*H*), 8.06 (s, 4 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.17, 22.96, 26.13, 30.43, 31.63, 32.30, 41.13, 75.72, 112.04, 120.93, 124.60, 124.74, 125.84, 126.79, 130.69, 135.90, 147.74, 155.53 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1389.80 [*M* - $C_{15}H_{12}$+H]$^+$, calcd monoisotopic peak ($^{12}C_{97}{}^1H_{106}{}^{14}N_4{}^{16}O_4$) 1389.8136, elemental analysis calcd (%) for $C_{112}H_{116}N_4O_4$ (1582.14): C 85.02, H 7.39, N 3.54; found C 85.08, H 7.42, N 3.56.

Compound 17. **3** (100 mg, 0.13 mmol) and anthracene (358 mg, 2.01 mmol) were dissolved in DCM (12.07 mL). After three freeze-thaw cycles the solution was irradiated with UV light for 12 hours. Afterwards the solvent of the turbid mixture was removed *in vacuo*. The crude mixture was purified by column chromatography (3:1 hexane/EtOAc then 1:1 hexane/EtOAc) and yielded 78.3 mg (45 %) of **17** as colourless solid. R_f = 0.32 (hexane/EtOAc 3:1); m.p. 178 – 179 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (d, 6 H, $^3J_{H,\,H}$ = 6.3 Hz, C*H*NH), 3.54 (br, 2 H, C*H*OH), 4.45 (d, 3 H, $^3J_{H,\,H}$ = 10.81 Hz, CH_{bridge}), 4.45 (br, 1 H, $^3J_{H,\,H}$ = 10.81 Hz, O*H*), 4.67 (d, 3 H, $^3J_{H,\,H}$ = 10.81 Hz, CH_{bridge}), 5.58 (s, 3 H, CH_{bridge}), 6.72 – 6.84 (m, 40 H, Ar*H*), 6.9 – 6.96 (m, 14 H, Ar*H*, N*H*), 7.03 – 7.0 (m, 6 H, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.43, 46.86, 53.44, 53.99, 54.22, 62.28, 66.24, 125.37, 125.45, 127.57, 126.38, 126.77, 126.94, 127.07, 127.65, 127.91, 175.76 ppm; MS (MALDI-FT, 3-HPA): *m/z* = 1280.5347 $[M + H]^+$, calcd monoisotopic peak ($^{12}C_{92}{}^1H_{70}{}^{14}N_3{}^{16}O_4$) 1280.5361, elemental analysis calcd (%) for $C_{92}H_{69}N_3O_4$ (1280.55): C 86.29, H 5.43, N 3.28; found C 86.42, H 5.63, N 3.31.

Compound dim-18. **18** (221 mg, 1 mmol) was dissolved in DCM (1 mL) and applied to the general dimerization protocol. 296 mg (67%) of the **dim 18** was obtained as yellowish solid. M.p. 216 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.64 (s, 6 H, CH_3), 3.75 (br, 2 H, CH_{bridge}), 3.78 (br, 4 H, C*H*NH), 6.86 – 6.92 (m, 8H), 7.07 (d, 4 H, $^3J_{H,\,H}$ = 4.5 Hz, Ar*H*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.91, 56.54, 56.69, 61.9, 125.41, 125.58, 127.53, 142.68, 143.43 (Ar*H*) ppm; MS (EI): *m/z* = 221.1198 $[M]^+$ calcd for $C_{16}H_{15}N$: 221.1204, elemental analysis calcd (%) for $C_{32}H_{30}N_2$ (442.59): C 86.84, H 6.83, N 6.33; found C 86.91, H 6.88, N 6.35.

Compound dim-19. The general dimerization protocol was applied to a solution of **19** (247 mg, 1 mmol) in dichloromethane (1 mL). 116 mg (47%) of **dim 19** was obtained as yellowish solid. M.p. 246 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.64 (s, 6 H, CH_3), 3.75 (br, 2 H, CH_{bridge}), 3.78 (br, 4 H, C*H*NH), 6.82 - 6.91 (m, 8 H, Ar*H*), 7.07 (d, 4 H, $^3J_{H,\,H}$ = 4.5 Hz, Ar*H*) ppm; ^{13}C ($CDCl_3$): δ = 45. 98, 51.47, 124.58, 125.45, 126.70, 127.05, 127.48, 132.45, 139.14, 144.66 ppm; MS (EI): *m/z* = 245.9995 $[M]^+$, calcd for $C_{14}H_8Cl_2$ 246.0003, elemental analysis calcd (%) for $C_{28}H_{16}Cl_4$ (494.24): C 68.04, H 3.26, Cl, 28.69; found C 68.09, H 3.28, N 28.63. Single crystal X-ray analysis of the sample recrystallized from $CDCl_3$. The molecular structure is shown in Figure S1.

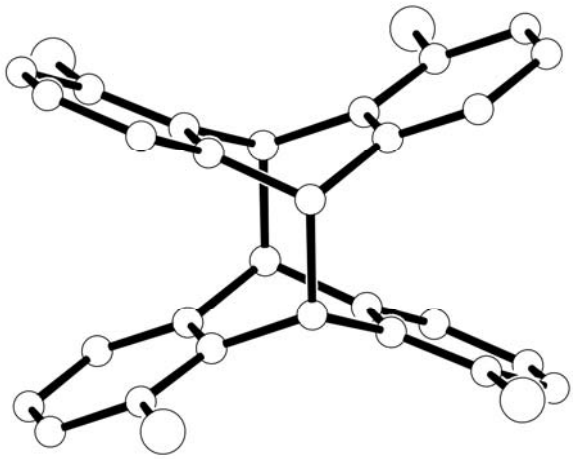

Figure S1**.** X-ray molecular structure of **dim-19**.

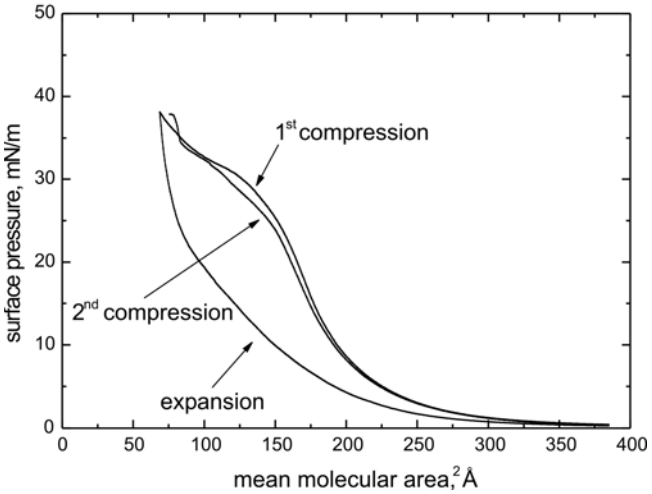

Figure S2. Surface pressure area isotherm of compound **16a** beyond the collapse pressure.

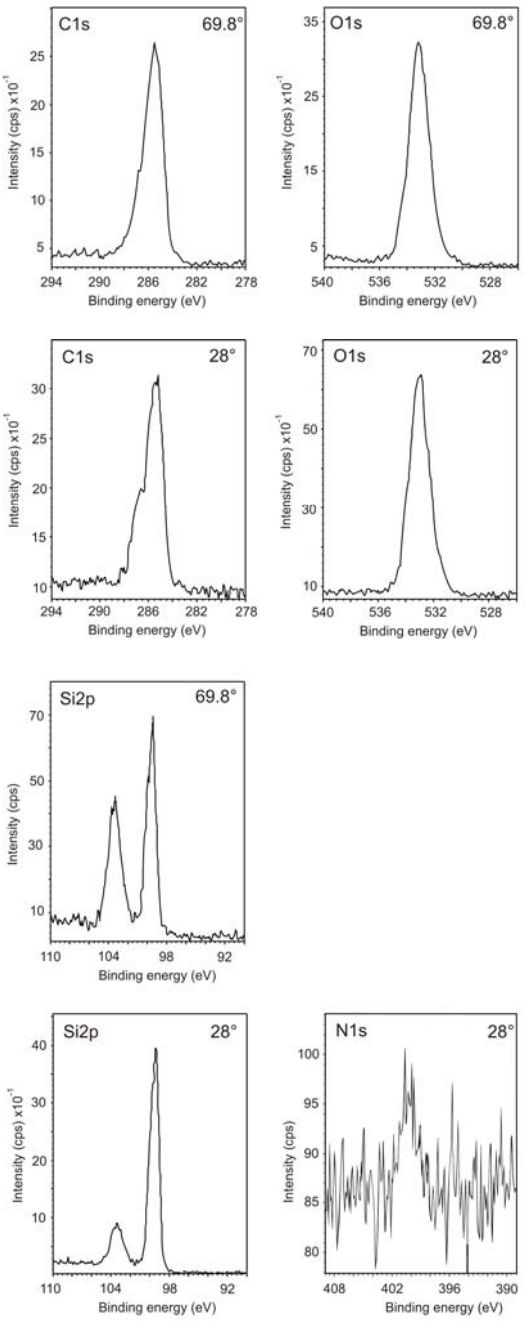

Figure S3. Detailed XPS spectra of C1s, O1s, N1s, and Si2p of non-polymerized monolayer of **16a** transferred on an oxidized silicon wafer.