Supporting Information
for
Synthesis and Association Behavior of Butadiyne-Bridged [4_4](2,6)Pyridinophane and [4_6](2,6)Pyridinophane Derivatives

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General. ^{1}H NMR (400 or 270 MHz) and ^{13}C NMR (100.5 or 67.5 MHz) spectra were recorded on a JEOL JNM-AL-400 or a JEOL JNM-GSX-270 spectrometer in $CDCl_3$ at 30 ˚C. The chemical shifts of ^{1}H NMR and ^{13}C NMR signals are quoted relative to internal $CHCl_3$ (δ = 7.26 and 77.0) or tetramethylsilane. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ) and interpretation multiplicity in the proton-coupled spectra deduced on the basis of the DEPT spectra (s = singlet, d = doublet, t = triplet, q = quartet). IR spectra were recorded as a KBr disk or a neat film on a Hitachi 260-10 spectrometer or a JASCO FTIR-410 spectrometer. FT-Raman spectra were obtained on a Bio-Rad FT-Raman II spectrometer at the Faculty of Science, Osaka University. UV-visible spectra were recorded on a Hitachi 220A spectrometer in $CHCl_3$ or toluene. Mass spectral analyses were performed on a JEOL JMS-DX303HF spectrometer. Elemental analyses were carried out by a Perkin-Elmer 2400II analyzer. Melting points were measured with a hot-stage apparatus. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent.

Octyl 2,6-Dichloro-4-isonicotinate (6). A 300 mL three-necked round-bottomed flask equipped with a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. To the flask, 2.49 g (13.0 mmol) of 2,6-dichloro-4-isonicotinic acid prepared by the reaction of citrazinic acid and phosphoryl chloride,[1] 5.07 g (39.0 mmol) of 1-octanol, 238 mg (1.95 mmol) of *N*,*N*-dimethylaminopyridine, and 40 mL of 1,2-dichloroethane were added in this order. A solution of 6.92 g (33.5 mmol) of 1,3-dicyclohexylcarbodiimide in 10 mL of 1,2-dichloroethane was added dropwise to the flask during 10 min at 0 ℃ and the solution was stirred for 5.5 h at ambient temperature. After removal of the resultant

dicyclohexylurea by filtration, the reaction mixture was washed with 100 mL of 1N HCl and 100 mL of brine and the organic layer was dried over $MgSO_4$. The solvent was evapolated, and the residue was chromatographed on silica gel to give 3.42 g (91%) of ester **6** as a pale yellow solid. decomp. 186 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.79 (s, 2H), 4.37 (t, *J* = 6.8 Hz, 2H), 1.79 (quintet, *J* = 6.8 Hz, 2 H), 1.47-1.29 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 ℃) δ 162.42 (s), 151.19 (s), 142.63 (s), 122.39 (d), 66.69 (t), 31.73 (t), 29.14 (t), 28.47 (t), 25.87 (t), 22.61 (t), 14.05 (q); IR (KBr) 1735, 1282, 766 cm^{-1}; MS (EI) *m/z* 303 (M^+).

Octyl 2,6-Bis[(trimethylsilyl)ethynyl]-4-isonicotinate (7).[2] A 1 L three-necked round-bottomed flask equipped with a reflux condenser, a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. To the flask, 45.7 g (150 mmol) of **6**, 34.2 g (349 mmol) of trimethylsilylacetylene, 3.3 g (13 mmol) of triphenylphosphine, 500 mL of triethylamine, and 1.2 g (2.1 mmol) of $Pd_2(dba)_3$•$CHCl_3$ (dba = dibenzylideneacetone)[3] were added and the pale yellow suspension was stirred at 70 ℃ for 1 day. After removal of the precipitate by filtration, the solvent was evaporated and the residue was chromatographed on silica gel (eluent: benzene/hexane = 3/7) to give 40.1 g (63%) of ester **7** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.89 (s, 2H), 4.35 (t, *J* = 6.9 Hz, 2H), 1.78 (quintet, *J* = 6.9 Hz, 2 H), 1.44-1.26 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.27 (s, 18H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 ℃) δ 163.76 (s), 144.05 (s), 138.28 (s), 125.61 (d), 102.46 (s), 96.64 (s), 66.28 (t), 31.76 (t), 29.18 (t), 29.13 (t), 28.57 (t), 25.91 (t), 22.64 (t), 14.11 (q), -0.32 (q); IR (neat) 2164, 1734, 1251, 762 cm^{-1}; MS (EI) *m/z* 427 (M^+).

Partial Deprotection of 7: Octyl 2-Ethynyl-6-(trimethylsilyl)ethynyl-4-isonicotinate (8) and Octyl 2,6-Diethynyl-4-isonicotinate. To a 500 mL three-necked round-bottomed flask equipped with a magnetic stirring bar and sealed with a rubber septum, 16.8 g (39.3 mmol) of **7**, 54 mg (0.39 mmol) of potassium carbonate, 60 mL of water, and 300 mL of THF were added and the solution was stirred at ambient temperature for 30 min. After the solvent was evaporated, 300 mL of ether was added, and the solution was washed with 100 mL of water and 100 mL of brine, and then the organic layer was dried over $MgSO_4$. After removal of solvent, the residue was chromatographed on silica gel (eluent: benzene/hexane = 9/1) to give 5.21 g (37%) of ester **8** as a pale yellow solid together with fully desilylated by-product,

octyl 2,6-diethynyl-4-isonicotinate (3.68 g, 33%), and the recovered starting material **7** (3.18 g, 19%). **8**: ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.92 (d, *J* = 1.5 Hz, 1H), 4.35 (t, *J* = 6.8 Hz, 2H), 3.21 (s, 1H), 1.78 (quintet, *J* = 6.9 Hz, 2 H), 1.44-1.26 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 ℃) δ 163.51 (s), 144.11 (s), 143.22 (s), 138.37 (s), 125.93 (d), 125.55 (d), 102.24 (s), 96.79 (s), 81.61 (d), 78.51 (s), 66.26 (t), 31.69 (t), 29.11 (t), 29.07 (t), 28.48 (t), 25.85 (t), 22.57 (t), 14.03 (q), -0.41 (q); IR (neat) 3308, 2115, 1732, 1223, 768 cm^{-1}; MS (EI) *m/z* 355 (M^+). **Octyl 2,6-Diethynyl-4-isonicotinate**: mp 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.96 (s, 2H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.23 (s, 2H), 1.78 (quintet, *J* = 6.8 Hz, 2 H), 1.47-1.25 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 ℃) δ 163.39 (s), 143.37 (s), 138.54 (s), 126.03 (d), 81.48 (d), 78.69 (s), 66.35 (t), 31.71 (t), 29.12 (t), 29.07 (t), 28.47 (t), 25.87 (t), 22.58 (t), 14.04 (q); IR (KBr) 3263, 2111, 1722, 1241, 771 cm^{-1}; MS (FAB) *m/z* 285 (M^++H). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.37; H, 7.33; N, 5.05. Found: C, 76.30; H, 7.47; N, 4.94.

TMS-protected 2mer 9. TMS-protected 2mer **9** was prepared by the Hay coupling.[4] A 100 mL two-necked round-bottomed flask equipped with a nitrogen inlet with a gas bubbler a magnetic stirring bar, and a rubber septum was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. To the flask, 2.56 g (25.9 mmol) of CuCl, 1.0 g (8.6 mmol) of *N, N, N', N'*-tetramethylethylenediamine, and 50 mL of acetone were added and the solution was stirred for 1 h at ambient temperature. After the solution was permitted to stand for a few minutes, a supernatant solution was employed as a Hay catalyst solution. Next, a 100 mL three-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. After 10.17 g (28.65 mmol) of **8** and 20 mL of acetone were added to the flask, the solution was stirred at ambient temperature while oxygen was bubbled from a inlet tube. A 30 mL-portion of Hay catalyst solution was added dropwise. After 48 h, the solvent was evaporated and the residue was chromatographed on silica gel (eluent: benzene/hexane = 7/3) to give 8.36 g (82%) of **9** as a red solid. mp 94-95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 7.97 (d, *J* = 1.5 Hz, 2H), 7.95 (d, *J* = 1.5 Hz, 2H), 4.36 (t, *J* = 6.9 Hz, 4H), 1.79 (quintet, *J* = 6.9 Hz, 4H), 1.45-1.26 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 6H), 0.29 (s, 18H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 °C) δ 163.55 (s), 144.62 (s), 142.67 (s), 138.62 (s), 126.60

(d), 102.14 (s), 100.54 (d), 97.48 (s), 80.44 (s), 74.12 (s), 66.51 (t), 31.81 (t), 29.22 (t), 29.17 (t), 28.58 (t), 25.95 (t), 22.68 (t), 14.13 (q), -0.34 (q); IR (KBr) 2156, 1726, 1222, 769 cm^{-1}; MS (FAB) *m/z* 710 (M^++H). Anal. Calcd for $C_{42}H_{56}N_2O_4Si_2$: C, 71.14; H, 7.96; N, 3.95. Found: C, 71.05; H, 8.16; N, 3.97.

Partial Deprotection of 9: Mono-protected 2mer 10 and 2mer 11. Mono-protected 2mer **10** and 2mer **11** were prepared in a similar manner as partial deprotection of **7** using 5.0 g (7.0 mmol) of **9** and 29 mg (0.2 mmol) of potassium carbonate in 75 mL of THF. The products were chromatographed on silica gel (eluent: benzene/hexane = 7/3) to give 1.87 g (44%) of mono-protected 2mer **10** as a reddish solid, 1.38 g (37%) of 2mer **11** as a reddish solid, and the recovered starting material **9** (0.77 g, 16%). **10**: mp 81-82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 8.01 (d, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.97 (d, *J* = 1.5 Hz, 1H), 7.95 (d, *J* = 1.5 Hz, 1H), 4.37 (t, *J* = 6.8 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.26 (s, 1H), 1.79 (quintet, *J* = 6.8 Hz, 4 H), 1.45-1.26 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 6H), 0.29 (s, 9H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 ℃) δ 163.55 (s), 163.41 (s), 144.64 (s), 143.87 (s), 142.86 (s), 142.62 (s), 138.80 (s), 138.64 (s), 126.64 (d), 126.60 (d), 102.12 (s), 97.52 (s), 81.44 (d), 80.56 (s), 79.05 (s), 74.26 (s), 74.02 (s), 66.59 (t), 66.53 (t), 31.81 (t), 29.22 (t), 29.17 (t), 28.57 (t), 25.96 (t), 22.68 (t), 14.13 (q), -0.34 (q); IR (KBr) 3310, 2156, 1730, 1225, 769 cm^{-1}; MS (FD) *m/z* 639 (M^++H). Anal. Calcd for $C_{39}H_{48}N_2O_4Si$: C, 73.55; H, 7.60; N, 4.40. Found: C, 73.61; H, 7.59; N, 4.38. **11**: mp 76-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.02 (d, *J* = 1.5 Hz, 2H), 7.99 (d, *J* = 1.5 Hz, 2H), 4.37 (t, *J* = 6.8 Hz, 4H), 3.26 (s, 2H), 1.79 (quintet, *J* = 6.8 Hz, 4H), 1.47-1.26 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 30 ℃) δ 163.40 (s), 143.89 (s), 142.81 (s), 138.81 (s), 127.07 (d), 126.69 (d), 81.43 (d), 80.36 (s), 79.08 (s), 74.17 (s), 66.60 (t), 31.82 (t), 29.23 (t), 29.18 (t), 28.57 (t), 25.92 (t), 22.68 (t), 14.14 (q); IR (KBr) 3272, 2116, 1734, 1223, 768 cm^{-1}; MS (FAB) *m/z* 566 (M^++H). Anal. Calcd for $C_{36}H_{40}N_2O_4$: C, 76.57; H, 7.14; N, 4.96. Found: C, 76.64; H, 7.15; N, 4.90.

Dibrominated 2mer 12. A 30 mL two-necked round-bottomed flask equipped with a nitrogen inlet with a gas bubbler, a magnetic stirring bar, and an inlet tube sealed with a rubber septum was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. To the flask was added 200 mg (0.28 mmol) of **11** and 8 mL of acetone followed by 19 mg (0.1 mmol) of silver nitrate. The apparatus was shielded from light with an aluminum foil, then 110 mg (0.62 mmol) of *N*-bromosuccinimide in 2 mL of acetone was added dropwise. After 2.5 h the solution

was poured into 20 mL of water and then extracted with chloroform (3 × 30 mL). The combined organic layer was washed with 20 mL of water and 20 mL of brine and the organic layer was dried over $MgSO_4$. After removal of solvent the product was purified by flash chromatography on silica gel to afford 117 mg of **12** as a brown solid (57% yield). mp 131-132 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 8.01 (t, *J* = 1.5 Hz, 2H), 7.94 (d, *J* = 1.5 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 4H), 1.78 (q, *J* = 6.8 Hz, 4H), 1.45-1.30 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 ℃) δ 163.39 (s), 144.18 (s), 142.78 (s), 138.86 (s), 126.89 (d), 126.60 (d), 80.34 (s), 78.63 (s), 74.17 (s), 66.61 (t), 54.53 (s), 31.83 (t), 29.24 (t), 29.19 (t), 28.58 (t), 25.98 (t), 22.69 (t), 14.15 (q); IR (KBr) 3075, 2207, 2156, 1739, 1223, 768 cm^{-1}; MS (FAB) *m/z* 721 (M^++H). Anal. Calcd for $C_{36}H_{38}Br_2N_2O_4$: C, 59.85; H, 5.30; N, 3.88. Found: C, 59.87; H, 5.31; N, 3.90.

TMS-protected Linear 4mer 13. TMS-protected linear 4mer **13** was prepared from mono-protected 2mer **10** (1.85 g, 3.28 mmol) by the Hay coupling[4] as described for the preparation of TMS-protected 2mer **9**. The product was purified by flash chromatography on silica-gel (eluent: benzene/chloroform = 1/1) to give 1.64 g of **13** as a reddish solid (89% yield). mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 8.05-8.04 (m, 4H), 7.98 (d, *J* = 1.4 Hz, 2H), 7.96 (d, *J* = 1.4 Hz, 2H), 4.38 (t, *J* = 6.8 Hz, 4H), 1.83-1.75 (m, 8H), 1.44-1.32 (m, 40H), 0.91-0.88 (m, 12H), 0.29 (s, 18H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 ℃) δ 163.53 (s), 163.22 (s), 144.65 (s), 143.26 (s), 143.14 (s), 142.58 (s), 138.90 (s), 138.65 (s), 127.52 (d), 127.49 (d), 126.62 (d), 102.11 (s), 97.54 (s), 80.79 (s), 80.37 (s), 80.03 (s), 74.58 (s), 73.94 (s), 66.70 (t), 66.53 (t), 31.83 (t), 31.80 (t), 29.22 (t), 29.18 (t), 28.58 (t), 25.98 (t), 25.95 (t), 22.68 (t), 14.14 (q), -0.31 (q); IR (KBr) 2925, 2856, 2155, 1732, 1223, 767 cm^{-1}; MS (FD) *m/z* 1273 (M^++H).

Deprotection of 13: Linear 4mer 14. Linear 4mer **14** was prepared in a similar manner as the partial deprotection of **7** using 25 mg (0.020 mmol) of **13** and 5 mg (0.04 mmol) of potassium carbonate in 5 mL of THF. The product was chromatographed on silica gel (eluent: chloroform) to give 18 mg (80%) of 4mer **14** as a brown solid. mp 108-109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 8.05-8.04 (m, 4H), 8.03 (d, *J* = 1.5 Hz, 2H), 7.99 (d, *J* = 1.5 Hz, 2H), 4.38 (t, *J* = 6.6 Hz, 4H), 4.37 (t, *J* = 6.6 Hz, 4H), 3.26 (s, 2H), 1.82-1.75 (m, 8H), 1.44-1.24 (m, 40H), 0.91-0.88 (m, 12H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 ℃) δ 163.40 (s), 163.22 (s),

143.92 (s), 143.23 (s), 142.78 (s), 138.93 (s), 138.83 (s), 127.53 (d), 127.51 (d), 81.43 (d), 80.60 (s), 80.38 (s), 80.15 (s), 79.31 (s), 78.94 (s), 74.50 (s), 74.40 (s), 66.72 (t), 66.61 (t), 31.83 (t), 29.24 (t), 29.19 (t), 28.58 (t), 25.99 (t), 22.69 (t), 14.16 (q); IR (KBr) 3264, 2155, 1732, 1223, 768 cm^{-1}; MS (FD) *m/z* 1128 (M^++H).

Cyclization of Linear 4mer 14: [4_4](2,6)Pyridinophane (4). [4_4](2,6)-Pyridinophane (**4**) was prepared by the intramolecular Eglinton coupling[5] of **14** using a mixture of pyridine and benzene (3:2, v/v) as a solvent. A 2 L three-necked round-bottomed flask equipped with a dropping funnel and an inlet tube sealed with a rubber septum was flushed with dry nitrogen and was flame dried under a flow of dry nitrogen. To the flask was added 485 mg (2.67 mmol) of $Cu(OAc)_2$ in 500 mL of the mixed solvent followed by 301 mg (0.267 mmol) of **14** in 200 mL of the mixed solvent through a Hershberg dropping funnel during 8 h. After 60 h the solvent was evaporated and the residue was chromatographed on silica gel to give 216 mg of a black solid. The product was purified by preparative HPLC separation to give 150 mg of **4** as a brown solid (50% yield). decomp. 168 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 7.92 (s, 8H), 4.37 (t, *J* = 6.9 Hz, 8H), 1.79 (quintet, *J* = 6.9 Hz, 8H), 1.48-1.26 (m, 40H), 0.90 (t, *J* = 6.9 Hz, 12H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 ℃) δ 163.29 (s), 143.35 (s), 139.07 (s), 125.04 (d), 82.17 (s), 74.72 (s), 66.59 (t), 31.79 (t), 29.21 (t), 29.16 (t), 28.54 (t), 25.96 (t), 22.65 (t), 14.11 (q); IR (KBr) 2153, 1731, 1254, 768 cm^{-1}; MS (FD) *m/z* 1126 (M^++H). Anal. Calcd for $C_{72}H_{76}N_4O_8$: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.21; H, 6.87; N, 4.74.

TMS-protected Linear 6mer 15. TMS-protected linear 6mer **15** was prepared by Vassela coupling[6] of dibrominated 2mer **12** and 2 equivalent of mono-protected 2mer **10**. 3.2 mg (0.0031 mmol) of $Pd_2(dba)_3$•$CHCl_3$,[3] 0.3 mg (0.002 mmol) of CuI, 3.8 mg (0.017 mmol) of trifurylphosphine, and 260 mg (0.408 mmol) of **10** were added to a 100 mL three-necked round-bottomed flask equipped with a Hershberg-type dropping funnel. The apparatus was degassed *in vacuo* and then it was purged with dry nitrogen. 0.15 mL (0.82 mmol) of 1,2,2,6,6-pentamethylpiperidine (PMP) in 3 mL of benzene was added and then 150 mg (0.21 mmol) of **12** and 0.04 mL (0.2 mmol) of PMP in 50 mL of benzene were added dropwise slowly through the dropping funnel during 5 h. The solution was stirred for 15 h and the solvent was evaporated to give a crude product. The product was purified by flash chromatography on silica gel followed by preparative HPLC separation to afford 180 mg of **15** as a brown solid (49% yield based on **12**). decomp. 134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 30 ℃) δ 8.06 (s, 4H), 8.05 (m, 4H), 7.99 (d, *J* = 1.5 Hz, 2H), 7.96 (d, *J* = 1.5 Hz, 2H), 4.38

(m, 12H), 1.81 (m, 12H), 1.36-1.30 (m, 60H), 0.90 (m, 18H), 0.29 (s, 18H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 °C) δ 163.46 (s), 163.14 (s), 163.12 (s), 144.61 (s), 143.21 (s), 143.12 (s), 143.08 (s), 142.52 (s), 138.88 (s), 138.86 (s), 138.61 (s), 127.51 (d), 127.45 (d), 127.43 (d), 126.61 (d), 126.57 (d), 102.08 (s), 97.49 (s), 80.76 (s), 80.37 (s), 80.34 (s), 80.32 (s), 79.99 (s), 74.54 (s), 74.37 (s), 74.33 (s), 73.89 (s), 66.66 (t), 66.49 (t), 31.78 (t), 29.19 (t), 29.13 (t), 28.53 (t), 25.94 (t), 25.91 (t), 22.64 (t), 14.09 (q), -0.39 (q); IR (KBr) 3073, 2229, 2155, 1733, 1224, 847 cm^{-1}; MS (FAB) *m/z* 1834 (M^+). Anal. Calcd for $C_{114}H_{132}N_6O_{12}Si_2$: C, 74.64; H, 7.25; N, 4.58. Found: C, 74.69; H, 7.36; N, 4.69.

Deprotection of 15: Linear 6mer 16. 100 mg (0.0545 mmol) of **15**, 5 mL of THF, and 0.02 mL of water were added to a 30 mL two-necked round-bottomed flask and the solution was stirred at ambient temperature. A mixture of 0.01 mL of acetic acid (0.2 mmol) and 1.2 mL of tetrabutylammonium fluoride (0.12 mmol) in THF (0.1 M) was added dropwise during 10 min. After 45 min the solution was evaporated to give a crude product, which was purified by flash chromatography on silica gel to give 74 mg of **16** as a purple solid (80% yield). decomp. 115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.05 (d, *J* = 1.4 Hz, 8H), 8.02 (d, *J* = 1.4 Hz, 2H), 7.99 (d, *J* = 1.4 Hz, 2H), 4.38 (m, 12H), 3.26 (s, 2H), 1.79 (m, 12H), 1.30 (m, 60H), 0.89 (m, 18H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 °C) δ 163.35 (s), 163.16 (s), 143.88 (s), 143.19 (s), 143.14 (s), 143.13 (s), 142.73 (s), 138.90 (s), 138.81 (s), 127.54 (d), 127.53 (d), 127.51 (d), 127.49 (d), 127.06 (d), 126.69 (d), 81.43 (d), 80.60 (s), 80.37 (s), 80.15 (s), 79.10 (s), 74.50 (s), 74.41 (s), 74.39 (s), 74.09 (s), 66.72 (t), 66.61 (t), 31.85 (t), 29.25 (t), 29.20 (t), 28.60 (t), 26.00 (t), 22.71 (t), 14.17 (q); IR (KBr) 3074, 2155, 2117, 1732, 1224, 951, 768 cm^{-1}; MS (FAB) m/z 1690 (M^+).

Cyclization of Linear 6mer 16: [4$_6$](2,6)Pyridinophane (5). [4$_6$](2,6)-Pyridinophane (**5**) was prepared by the intramolecular Eglinton coupling[5] of **16** as described for the preparation of **4**. The product was purified by preparative HPLC to afford 64 mg of **5** as a brown solid (29% yield from **15**). decomp. 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.03 (s, 12H), 4.38 (t, *J* = 6.8 Hz, 12H), 1.79 (q, *J* = 6.8 Hz, 12H), 1.45-1.31 (m, 60H), 0.90 (t, *J* = 6.8 Hz, 18H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 30 °C) δ 163.30 (s), 143.24 (s), 138.83 (s), 127.13 (d), 80.32 (s), 74.30 (s), 66.66 (t), 31.84 (t), 29.24 (t), 29.19 (t), 28.58 (t), 25.99 (t), 22.69 (t), 14.15 (q); IR (KBr) 2155, 1735, 1255, 768 cm^{-1}; FT-Raman 2232, 1589, 1549, 977 cm^{-1}; UV

($CHCl_3$, 30 ℃) λ_{max} (log ε) 361 (5.13), 346 (5.06), 305 (4.85), 287 (4.88), 245 (5.06) nm; MS (FAB) *m/z* 1688 (M^++H).

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