Synthesis of Multilayered [3.3](3,5)Pyridinophanes[1]

Masahiko Shibahara,*[a] Motonori Watanabe,[b] Kazuhiro Aso,[a] Teruo Shinmyozu*[b]

[a] Department of Chemistry, Faculty of Education and Welfare Science, Oita University, 700 Dannoharu, Oita 870-1192, Japan
Fax +81(97)5547553; E-mail: mshiba@cc.oita-u.ac.jp

[b] Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan
E-mail: shinmyo@ms.ifoc.kyushu-u.ac.jp

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Abstract: Two- to four-layered [3.3](3,5)pyridinophanes (PyPs) have been synthesized by the (4-tolylsulfonyl)methyl isocyanide (TosMIC) method. The coupling reaction between 3,5-bis[2-isocyano-2-(4-tolylsulfonyl)ethyl]pyridine (TosMIC adduct) and bis(chloromethyl) or tetrakis(bromomethyl) compounds in the presence of sodium hydride in *N*,*N*-dimethylformamide or sodium hydroxide and tetrabutylammonium iodide under high-dilution conditions gave the two-layered dione or three- and four-layered tetraones. Wolff–Kishner reduction of the ketones afforded the desired two- to four-layered [3.3](3,5)PyPs. The structure of the dione units take an *anti* geometry whereas the cyclophane units take a *syn* geometry in solution.

Key words: cyclophanes, pyridines, coupling reaction, ketones, Wolff–Kishner reduction

[3.3]Metapyridinophanes (MPyPs) are composed of two pyridine rings and two three-atom bridges connected to them. Among the various types of [3.3]MPyPs, the [3.3](2,6)PyPs have been studied in detail and the 2,11-diaza,[2] dithia,[3] dioxa,[4] and diselena derivatives[5] have been synthesized along with all the carbon parent cyclophanes[6] (Figure 1). These PyPs have served as ligands for transition-metal complexes, and various kinds of metal complexes have been prepared.[5,7] Their conformational isomerism has also attracted much attention.[8] In contrast, a limited number of [3.3](3,5)PyP are known to date, mainly due to the instability of the coupling precursor, 3,5-bis(halomethyl)pyridine. In our recent preparation of 2,11-diaza[3.3](3,5)PyP, freshly prepared 3,5-bis(chloromethyl)pyridine was used for the coupling reaction.[9] One of the major advantages of the [3.3](3,5)PyPs over the [3.3](2,6)PyPs is the potential ability to form self-assembled supramolecules upon coordination, because the cyclophanes take *syn* geometry and the nitrogen lone pair electrons can readily coordinate to metals without steric hindrance by the bridges. For example, the formation of the double-decker type 2:2 complexes has been reported in 2,11-diaza-[10] and dithia[3.3](3,5)PyPs.[11]

In previous papers, we reported the synthesis of multilayered [3.3]cyclophanes by the (4-tolylsulfonyl)methyl isocyanide (TosMIC) method (metacyclophanes; MCPs)[12] and (4-ethylphenylsulfonyl)methyl isocyanide (EbsMIC) method (paracyclophanes; PCPs).[13] Therefore, multilayered MCPs incorporating pyridine rings at both ends may form larger supramolecules upon complexation with the transition metals and new types of supramolecules may serve as catalysts, inclusion hosts, and nanometer-scale materials. We now report the synthesis of two- to four-layered [3.3](3,5)PyPs **1**–**3** and their structures in solution by ^{1}H NMR studies.

[3.3](2,6)PyPs X = CH_2, NH, O, S, Se

[3.3](3,5)PyPs Y = NH, S

Figure 1 [3.3](2,6)- and [3.3](3,5)Pyridinophanes

Multilayered [3.3](3,5) PyPs **1**–**3** were synthesized by the TosMIC method in the critical coupling reaction (Scheme 1). The synthetic key intermediates for the synthesis of multilayered PyPs are bis(chloromethyl)pyridine **4**[9] and its TosMIC adduct **6**. 3,5-Bis(chloromethyl)pyridine (**4**) was synthesized by chlorination of 3,5-lutidine with *N*-chlorosuccinimide in carbon tetrachloride followed by column chromatography on silica gel (*n*-hexane–EtOAc, 3:1; $R_f = 0.20$) to give **4** in 32% yield. The chloride **4** was immediately reacted with (4-tolylsulfonyl)methyl isocyanide (TosMIC, **5**) under phase-transfer conditions, and the crude product was purified by column chromatography on silica gel (EtOAc–*n*-hexane, 3:2; $R_f = 0.34$) to give the TosMIC adduct **6** in 14% yield. The reason for the relatively low yield of the TosMIC adduct **6** may be ascribed to the instability of the chloride **4**. 3,5-Bis(chloromethyl)pyridine (**4**) was coupled with the TosMIC adduct **6** in the presence of sodium hydride in *N*,*N*-dimethylformamide at room temperature for 24 hours under nitrogen, followed by hydrolysis of the cyclic adduct with concentrated hydrochloric acid to give the two-layered dione **7** in 35% yield. Wolff–Kishner reduction of **7** and purification by column chromatography on silica gel (CH_2Cl_2–EtOH, 9:1; $R_f = 0.46$) afforded the two-layered PyP **1** in 93% yield. Thus, the parent [3.3](3,5)PyP has been synthesized for the first time, and successful isolation of the TosMIC adduct **6** was a key step in the synthesis of the multilayered [3.3](3,5)PyPs.

Tetrakis(bromomethyl) compounds **8** and **10** are versatile synthetic intermediates for the one-pot synthesis of three- and four-layered [3.3]MCPs, respectively.[12] 1,2,4,5-Tetrakis(bromomethyl)benzene (**8**) was coupled with the

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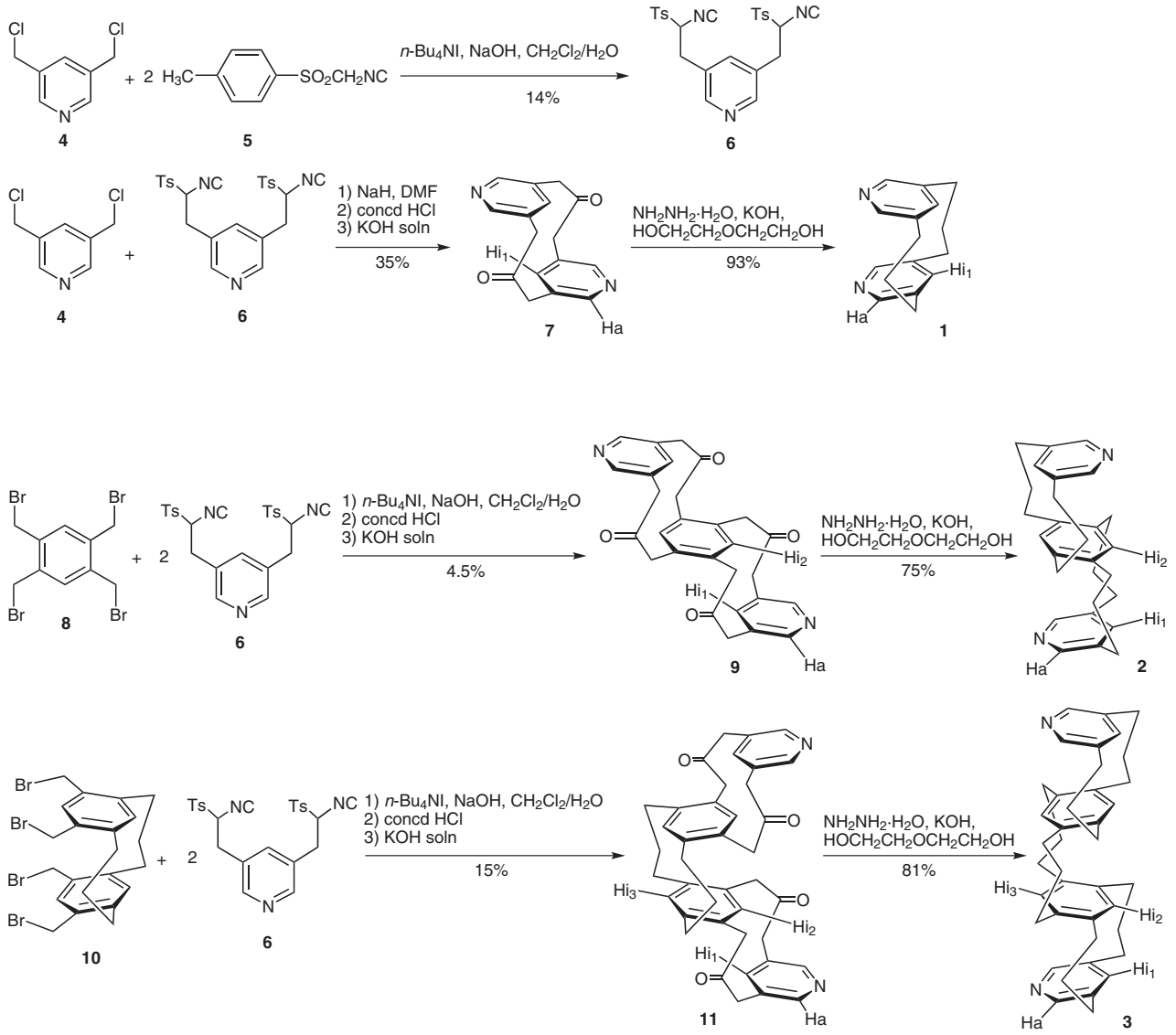

Scheme 1 Synthetic route to two- to four-layered [3.3](3,5)pyridinophanes **1**–**3**

TosMIC adduct **6** in the presence of sodium hydroxide and tetrabutylammonium iodide in a mixture of dichloromethane and water under phase-transfer conditions at reflux, followed by hydrolysis with concentrated hydrochloric acid to provide the desired three-layered tetraone **9** in 4.5% yield. The Wolff–Kishner reduction of the tetraone **9** gave the three-layered [3.3](3,5)PyP **2** in 75% yield after purification by column chromatography (silica gel, CH_2Cl_2–EtOH, 9:1; $R_f = 0.46$). A similar coupling reaction of 5,7,14,16-tetrakis(bromomethyl)[3.3]MCP **10** prepared by the one-step bromomethylation of [3.3]MCP[12] with the TosMIC adduct **6** afforded the four-layered tetraone **11**, which was converted into the four-layered [3.3](3,5)PyP **3** by Wolff–Kishner reduction in 81% yield after purification by column chromatography (silica gel, CH_2Cl_2–EtOH, 9:1; $R_f = 0.53$).

It is known that [3.3]MCP and its dione adopt different *syn* and *anti* geometry as stable conformers in solution, respectively, and we have studied the conformational behavior of the [3.3]MCPs and related systems in detail.[13b,14] Moreover, we have recently reported the structural properties of the multilayered [3.3]MCPs in solution and in the solid state,[12] in which the [3.3]MCP moiety takes the *syn* geometry whereas the [3.3]MCP-dione moiety takes the *anti* geometry. This indicated that the original stable conformations are maintained even in the multilayered [3.3]MCPs. Similarly, the [3.3]MCP units assume *syn* geometry in multilayered [3.3](3,5)PyPs **1**–**3** (Figure 2). The Hi_1 protons of the two-layered **1** appear at the normal position, which is comparable to that of [3.3]MCP, while the inner aromatic protons, Hi_2 in the three-layered **2** and Hi_2 and Hi_3 in the four-layered **3**, are moderately shielded due to the diamagnetic ring current effect of the stacked aromatic rings. This indicates the *syn-syn* and *syn-syn-syn* geometries for **2** and **3**, respectively. All the aromatic protons of **2** and **3** are assigned on the basis of their NOESY spectra, in which the correlations are observed between Hi_1–Hi_2, Ha–Hb, and Ha–Hc in the three-layered **2** (Figure 3). As for the four-layered **3**, the correlations are

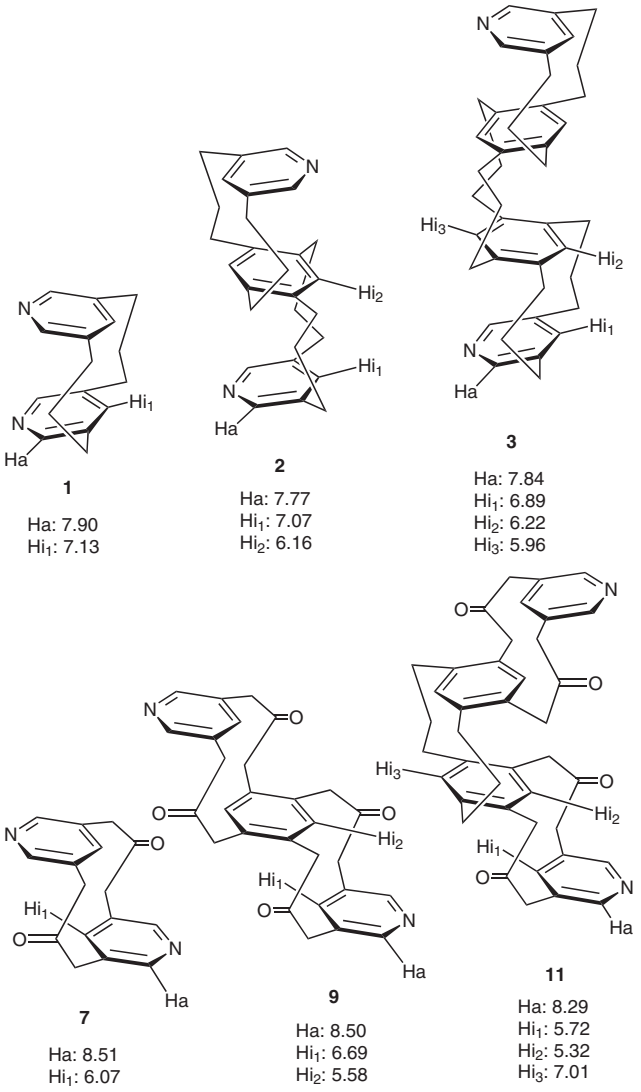

Figure 2 Selected ^{1}H NMR data of the aromatic protons of multilayered [3.3](3,5)PyPs and diones (δ, 300 MHz, $CDCl_3$)

observed between Hi_1–Hi_2, Ha–Hb, and Ha–Hc, while the correlation between Hi_1–Hi_3 is not observed (Figure 4). These results suggest the all-*syn* geometries for **2** and **3**. In contrast, multilayered [3.3](3,5)PyPs with dione units take an *anti* geometry as shown in Hi_1 in the two-layered **7**, Hi_1 and Hi_2 in the three-layered **9**, and Hi_1 and Hi_2 in the four-layered **11** due to the ring current effect of the faced aromatic rings, and this suggests *anti*, *anti-anti*, and *anti-syn-anti* geometries for **7**, **9**, and **11**, respectively. Thus multilayered [3.3]PyPs take structures similar to the corresponding multilayered [3.3]MCPs in solution.

In conclusion, we have synthesized the TosMIC adduct of 3,5-bis(chloromethyl)pyridine **6**, and the coupling of **6** with the bis- or tetrakis(halomethyl) compounds **4**, **8**, and **10** in the presence of sodium hydride in *N*,*N*-dimethylformamide or sodium hydroxide and tetrabutylammonium iodide in a mixture of dichloromethane and water under phase-transfer conditions gave the two- to four-layered [3.3](3,5)PyPs **1**–**3**, respectively. Similar to the structure of the multilayered [3.3]MCPs in solution, multilayered [3.3](3,5)PyPs **1**–**3** take the all-*syn* conformation, while the [3.3](3,5)PyP-dione moieties in **7**, **9**, and **11** assume *anti* geometry. Currently, we are investigating their structures in the solid state, complexation behavior, and conformational analysis, and these results will be reported elsewhere.

All melting points were measured on a Stuart Scientific Melting Point Apparatus SMP3, and are uncorrected. The ^{1}H and ^{13}C NMR spectra were measured using Jeol JNM-AL300, Jeol JNM-ECA600, and Bruker ARX-300 spectrometers; internal reference was TMS and the solvent was $CDCl_3$ or CD_2Cl_2 unless otherwise noted. The MS (FAB-MS, *m*-nitrobenzyl alcohol) were obtained using a Jeol JMS-SX/SX 102A mass spectrometer. The IR spectra were measured with a Nicolet Impact 400D spectrophotometer. The elemental analyses were performed by the Service Centre of the Elementary Analysis of Organic Compounds affiliated with the Faculty of Science, Kyushu University.

The analytical TLC was performed on Silica gel 60 F_{254} Merck. Column chromatography was performed on Kanto silica gel 60N (63–210 μm).

All solvents and reagents were of reagent quality, commercially purchased, and used without further purification, except as noted. 3,5-Bis(chloromethyl)pyridine[9] and TosMIC (except for the use of dioxane in place of DME)[15] were prepared according to the literature procedures.

3,5-Bis[2-isocyano-2-(4-tolylsulfonyl)ethyl]pyridine (6)

A mixture of *n*-Bu_4NI (0.73 g), CH_2Cl_2 (50 mL), and NaOH (8 g) dissolved in H_2O (32 mL) was stirred in an ice bath. To the mixture was added in one portion to a soln of TosMIC (**5**, 7.33 g, 37.5 mmol) in CH_2Cl_2 (40 mL). After 30 min, to the mixture in an ice bath was added freshly prepared chloride **4** (1.80 g, 10.2 mmol) in CH_2Cl_2 (50 mL) in one portion and the mixture was stirred for ca. 10 h in the ice bath. The mixture was then allowed to warm up to r.t. overnight. The mixture was washed with H_2O, dried ($MgSO_4$), filtered, and concentrated to a volume of ca. 30 mL at 25 °C. The concentrate was purified by column chromatography (silica gel, CH_2Cl_2 then EtOAc–hexane, 3:2; R_f = 0.34). The eluate was concentrated to a volume of ca. 30 mL, then CCl_4 was added (100 mL). The soln was concentrated to a volume of ca. 30 mL at 35 °C. The precipitate was collected by filtration and suspended in a small amount of cold acetone. The insoluble solid was collected by filtration to give the TosMIC adduct **6** (721 mg, 14%) as a white powder; mp 105 °C (dec).

IR (KBr): 2136, 1333, 1151 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 6 H, CH_3), 3.07 (dd, *J* = 14.0, 11.2 Hz, 2 H, CH_2CH), 3.61 (dd, *J* = 14.1, 3.2 Hz, 2 H, CH_2CH), 4.58 (dd, *J* = 11.1, 3.3 Hz, 2 H, CH_2CH), 7.46 (d, *J* = 8.0 Hz, 4 H, TsH), 7.56 (t, *J* = 2.1 Hz, 1 H, PyH), 7.90 (dd, *J* = 6.7, 1.6 Hz, 4 H, TsH), 8.53 (d, *J* = 2.1 Hz, 2 H, PyH).

^{13}C NMR (150 MHz, CD_2Cl_2): δ = 22.0, 32.3, 73.6, 129.9, 130.4, 130.8, 131.3, 138.2, 147.8, 150.6, 167.1.

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{24}N_3O_4S_2$: 494.1208; found: 494.1206.

Two-Layered [3.3](3,5)Pyridinophane (1)

To a mixture of NaH (60%, 0.25 g, 10.4 mmol) and DMF (80 mL) was dropwise added a mixture of chloride **4** (317 mg, 1.80 mmol) and TosMIC adduct **6** (887 mg, 1.80 mmol) dissolved in DMF (200 mL) at r.t. over a period of 7 h and the mixture was stirred at r.t. for an additional 16 h. The solvent was removed under reduced pressure and MeOH was added to the residue and the insoluble solid was

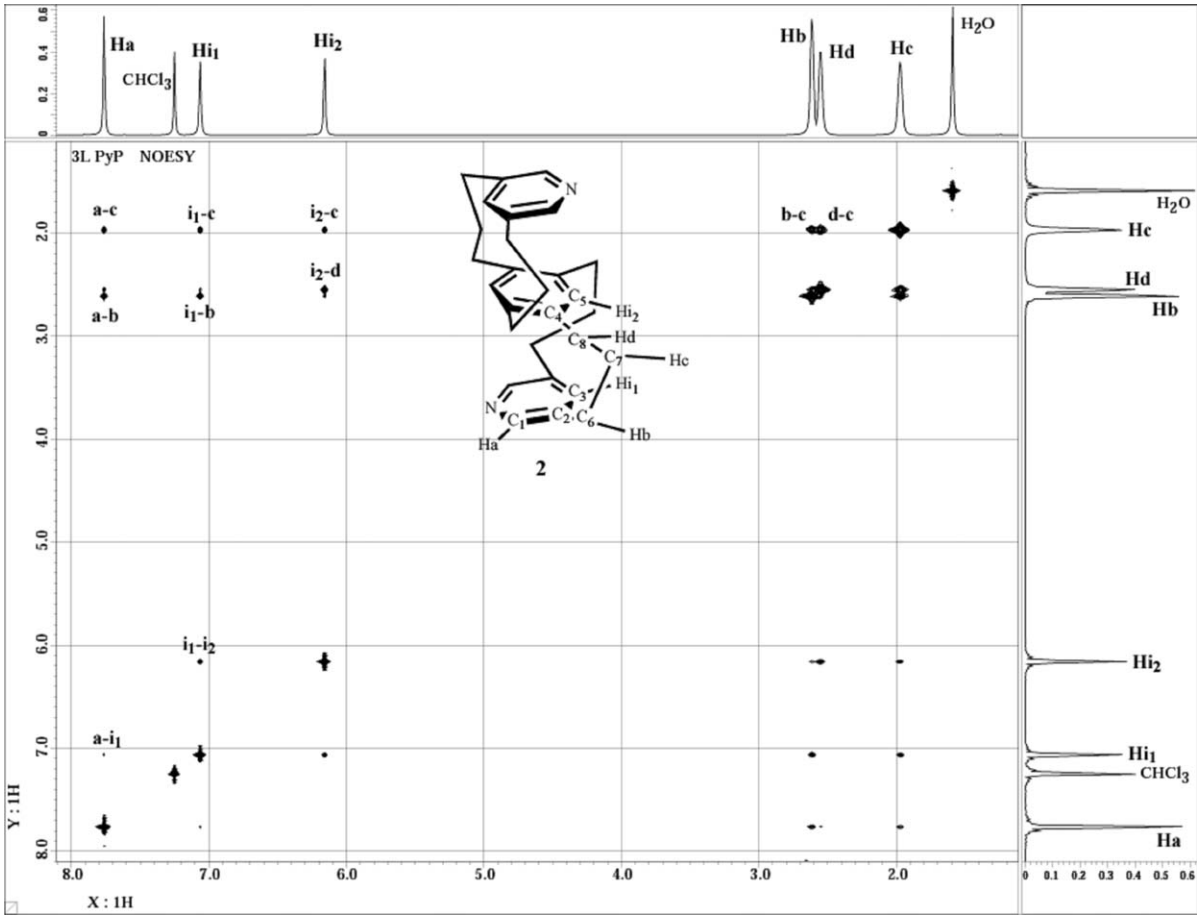

Figure 3 NOESY spectrum of three-layered [3.3](3,5)pyridinophane **2**

collected by filtration to give the cyclic TosMIC adduct as a pale brown powder.

To a mixture of the cyclic TosMIC adduct and CH_2Cl_2 (150 mL) was added concd HCl (5 mL) and it was stirred at r.t. After 3 h, KOH (10 g) dissolved in H_2O (30 mL) was added and the mixture was stirred at r.t. for 1 h. The mixture was extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with H_2O, dried ($MgSO_4$), and concentrated to dryness. The resulting residue was washed with acetone to give the dione **7** (169 mg, 35% for two steps) as colorless needles ($CHCl_3$); mp 212 °C (dec).

IR (KBr): 1698 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 8 H, CH_2COCH_2), 6.07 (t, *J* = 2.1 Hz, 2 H, ArH), 8.51 (d, *J* = 2.1 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.5, 129.0, 142.6, 149.8, 203.4.

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_2$: 267.1134; found: 267.1131.

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.09; H, 5.32; N, 10.48.

A mixture of the dione **7** (85 mg, 0.319 mmol), 98% $NH_2NH_2 \cdot H_2O$ (5 mL), KOH (820 mg), and diethylene glycol (20 mL) was heated at 130 °C for 3.5 h and then at 200 °C for 2 h with stirring. After cooling, the mixture was poured into ice water and extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with H_2O, dried ($MgSO_4$), and concentrated to dryness. Purification of the residue by column chromatography (silica gel, CH_2Cl_2–EtOH, 9:1; R_f = 0.46) produced the two-layered pyridinophane **1** (71 mg, 93%) as colorless prisms (acetone–THF); mp 241 °C (dec).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.0–2.2 (m, 4 H, $CH_2CH_2CH_2$), 2.76 (t, *J* = 5.8 Hz, 8 H, $CH_2CH_2CH_2$), 7.13 (t, *J* = 1.9 Hz, 2 H, ArH), 7.90 (d, *J* = 1.9 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3, 33.4, 134.7, 134.0, 147.5.

HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{16}H_{19}N_2$: 239.1548; found: 239.1549.

Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.38; H, 7.57; N, 11.77.

Three-Layered [3.3](3,5)Pyridinophane (2)

A mixture of *n*-Bu_4NI (1.50 g), NaOH (25 g) dissolved in H_2O (75 mL) and CH_2Cl_2 (800 mL) was heated to reflux with stirring. To the mixture was dropwise added a mixture of tetrabromide **8** (758 mg, 1.69 mmol) and TosMIC adduct **6** (1.67 g, 3.38 mmol) in CH_2Cl_2 over a period of 11 h, and the mixture was refluxed for an additional 11 h. The cooled mixture was washed with H_2O and concentrated to a volume of ca. 200 mL.

To the concentrate was added concd HCl (50 mL) and the mixture was stirred at r.t. After 3.5 h, 3 M HCl (200 mL) was added in one portion and the mixture was stirred at r.t. for 1.5 h. The aqueous soln was basified by the addition of NaOH and the precipitate was filtered. The crude product was suspended in $CHCl_3$ (200 mL) at reflux and filtered. The filtrate was concentrated to dryness, suspended in a small amount of acetone and pyridine and sonicated. The insoluble solid was recrystallized ($CHCl_3$) to give the tetraone **9** (34.3 mg, 4.5%) as an ivory powder ($CHCl_3$); mp 250 °C (dec).

IR (KBr): 1701 cm^{-1}.

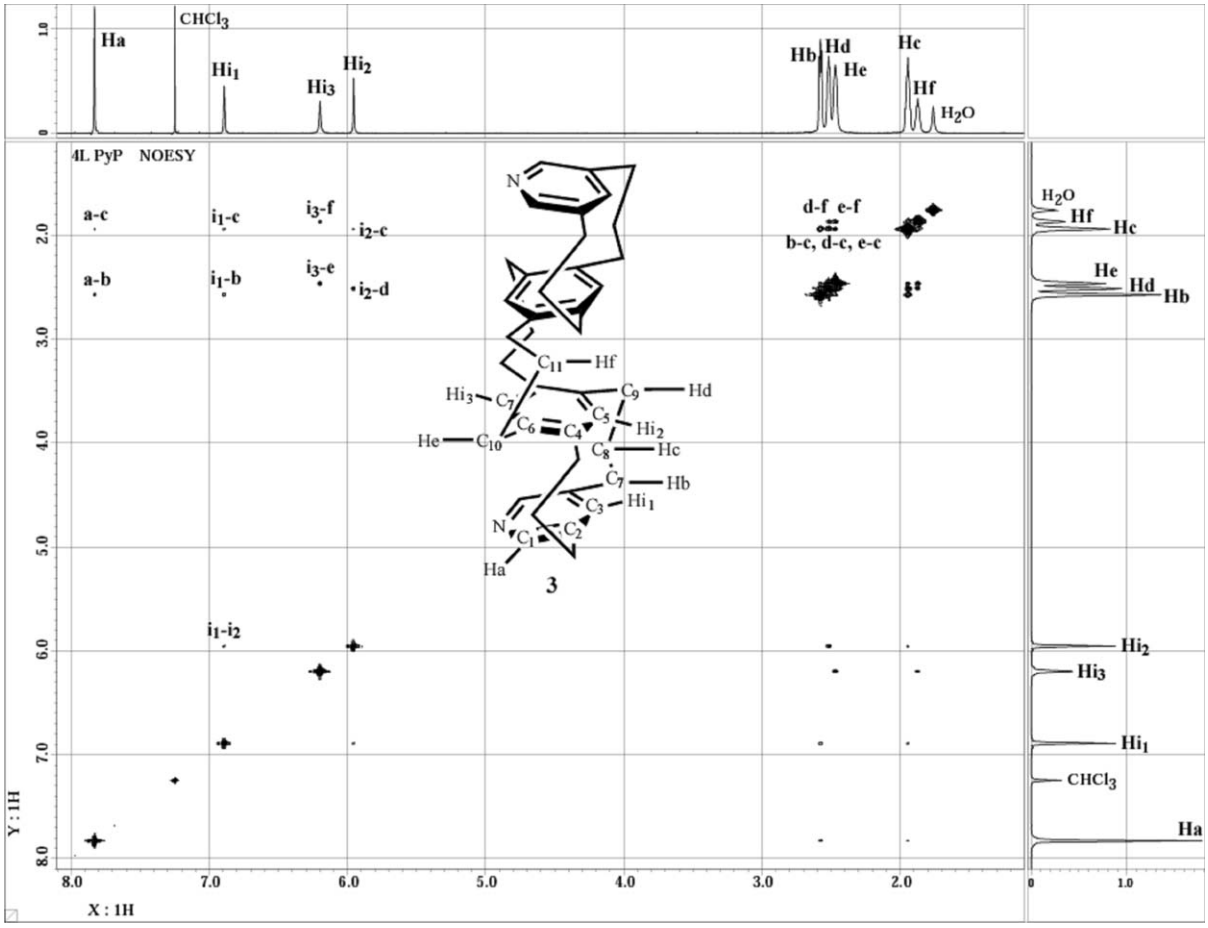

Figure 4 NOESY spectrum of four-layered [3.3](3,5)pyridinophane **3**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 8 H, CH_2COCH_2), 3.69 (s, 8 H, CH_2COCH_2), 5.58 (s, 2 H, Hi_2), 6.69 (d J = 2.1 Hz, 2 H, Hi_1), 8.50 (d, J = 2.1 Hz, 4 H, Ha).

HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{28}H_{25}N_2O_4$: 453.1814; found: 453.1812.

A mixture of the tetraone **9** (65.8 mg, 0.145 mmol), KOH (2 g), 98% $NH_2NH_2{\cdot}H_2O$ (5 mL), and diethylene glycol (25 mL) was heated at 130 °C for 12 h and then at 200 °C for 4 h with stirring. After cooling, the mixture was poured into ice water and extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with brine, dried ($MgSO_4$), and concentrated to dryness. Purification of the residue by column chromatography (silica gel, CH_2Cl_2–EtOH, 9:1; R_f = 0.46) produced the three-layered pyridinophane **2** (43.3 mg, 75%) as a white powder (CH_2Cl_2–acetone); mp 285 °C (dec).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.9–2.1 (m, 8 H, $CH_2CH_2CH_2$), 2.5–2.7 (m, 16 H, CH_2CH_2CH_2), 6.17 (s, 2 H, Hi_2), 7.08 (s, 2 H, Hi_1), 7.78 (s, 4 H, Ha).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 27.8, 32.7, 33.5, 134.0, 134.9, 135.4, 140.1, 146.7.

HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{28}H_{33}N_2$: 397.2644; found: 397.2640.

Anal. Calcd for $C_{28}H_{32}N_2$: C, 84.80; H, 8.13; N, 7.06. Found: C, 84.77; H, 8.03; N, 7.07.

Four-Layered [3.3](3,5)Pyridinophane (3)

A mixture of n-Bu_4NI (0.75 g), NaOH (10 g) dissolved in H_2O (50 mL) and CH_2Cl_2 (450 mL) was heated to reflux with stirring. To the mixture was dropwise added a mixture of tetrabromide **10** (489 mg, 0.804 mmol) and TosMIC adduct **6** (800 mg, 1.62 mmol) in CH_2Cl_2 over a period of 7 h, and the mixture was refluxed for an additional 12 h. The cooled mixture was washed with H_2O and concentrated to a volume of ca. 200 mL.

To the concentrate was added concd HCl (15 mL) and the mixture was stirred at r.t. After 4 h, KOH (20 g) dissolved in H_2O (80 mL) was added in one portion and the mixture was stirred for 4.5 h at r.t. The mixture was then extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with H_2O, dried ($MgSO_4$), and concentrated to dryness. The residue was suspended in acetone and collected by filtration to give the crude ketone, which was suspended in pyridine and the insoluble solid was recrystallized ($CHCl_3$) to give the pure tetraone **11** (68 mg, 15%) as colorless needles ($CHCl_3$); mp 250 °C (dec).

IR (KBr): 1702 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.9–2.1 (m, 4 H, $CH_2CH_2CH_2$), 2.81 (t, J = 5.5 Hz, 8 H, $CH_2CH_2CH_2$), 3.36 (s, 16 H, CH_2COCH_2), 5.32 (s, 2 H, Hi_2), 5.72 (t, J = 2.0 Hz, 2 H, Hi_1), 7.01 (s, 2 H, Hi_3), 8.29 (d, J = 2.0 Hz, 4 H, Ha).

HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{40}H_{39}N_2O_4$: 611.2910; found: 611.2924.

A mixture of the tetraone **11** (142 mg, 0.233 mmol), 98% $NH_2NH_2{\cdot}H_2O$ (8 mL), and diethylene glycol (25 mL) was heated at 130 °C with stirring. After 20 h, KOH (2 g) was added and heated at 200 °C for 6 h with stirring. After cooling, the mixture was poured into ice water and extracted with CH_2Cl_2. The CH_2Cl_2 soln was washed with brine, dried ($MgSO_4$), and concentrated to dryness. Purification of the residue by column chromatography (silica

gel, CH_2Cl_2–EtOH, 9:1; R_f = 0.53) produced the four-layered pyridinophane **3** (105 mg, 81%) as colorless prisms (CH_2Cl_2–acetone); mp 245 °C (dec).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.8–2.0 (m, 12 H, $CH_2CH_2CH_2$), 2.4–2.7 (m, 24 H, $CH_2CH_2CH_2$), 5.97 (s, 2 H, Hi_2), 6.21 (s, 2 H, Hi_3), 6.91 (s, 2 H, Hi_1), 7.84 (d, *J* = 1.5 Hz, 4 H, Ha).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.2, 27.7, 32.4, 32.7, 33.2, 134.0, 134.4, 134.8, 134.8, 135.8, 140.4, 146.8.

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{40}H_{47}N_2$: 555.3739; found: 555.3739.

Anal. Calcd for $C_{40}H_{46}N_2$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.35; H, 8.34; N, 5.01.

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References

(1) Multilayered [3.3]Cyclophanes, Part 4. For parts 1, 2, and 3, see refs. 12, 13a and 13b.
(2) (a) Bottino, F.; Grazia, M. D.; Finocchiaro, P.; Fronczek, F. R.; Mamo, A.; Pappalardo, S. *J. Org. Chem.* **1988**, *53*, 3521. (b) Takemura, H.; Wen, G.; Shinmyozu, T. *Synthesis* **2005**, 2845.
(3) Vögtle, F.; Schunder, L. *Chem. Ber.* **1969**, *102*, 2677.
(4) Newcomb, M.; Timko, J. M.; Walba, D. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6392.
(5) Muralidharan, S.; Hojjatie, M.; Firestone, M.; Freiser, H. *J. Org. Chem.* **1989**, *54*, 393.
(6) Shinmyozu, T.; Hirai, Y.; Inazu, T. *J. Org. Chem.* **1986**, *51*, 1551.
(7) (a) Fronczek, F. R.; Mamo, A.; Pappalardo, S. *Inorg. Chem.* **1989**, *28*, 1419. (b) Sakaba, H.; Kabuta, C.; Horino, H.; Arai, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1822. (c) Krüger, H.-J. *Chem. Ber.* **1995**, *128*, 531. (d) Koch, W. O.; Barbieri, A.; Grodzicki, M.; Schünemann, V.; Trautwein, A. X.; Krüger, H.-J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 422. (e) Kelm, H.; Krüger, H.-J. *Eur. J. Inorg. Chem.* **1998**, 1381. (f) Sciarone, T.; Hoogboom, J.; Schlebos, P. P. J.; Budzelaar, P. H. M.; Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2002**, 457. (g) Albelta, B.; Carina, R.; Policar, C.; Poussereau, S.; Cano, J.; Guilhem, J.; Tchertanov, L.; Blondin, G.; Delroisse, M.; Girerd, J.-J. *Inorg. Chem.* **2005**, *44*, 6959. (h) Moriguchi, T.; Kitamura, S.; Sakata, K.; Tsuge, A. *Polyhedron* **2001**, *20*, 2315.
(8) Sako, K.; Tatemitsu, H.; Onaka, S.; Takemura, H.; Osada, S.; Wen, G.; Rudzinski, J. M.; Shinmyozu, T. *Liebigs Ann.* **1996**, 1645.
(9) Satou, T.; Shinmyozu, T. *J. Chem. Soc., Perkin Trans. 2* **2002**, 393.
(10) Satou, T.; Sabae, M.; Iizuka, S.; Akita, M.; Shinmyozu, T. unpublished results.
(11) Tsuge, A.; Matsubara, A.; Moriguchi, T.; Sei, Y.; Yamaguchi, K. *Tetrahedron Lett.* **2006**, *47*, 6607.
(12) Shibahara, M.; Watanabe, M.; Iwanaga, T.; Ideta, K.; Shinmyozu, T. *J. Org. Chem.* **2007**, *72*, 2865.
(13) (a) Shibahara, M.; Watanabe, M.; Iwanaga, T.; Matsumoto, T.; Ideta, K.; Shinmyozu, T. *J. Org. Chem.* **2008**, *73*, 4433. (b) Muranaka, A.; Shibahara, M.; Watanabe, M.; Matsumoto, T.; Shinmyozu, T.; Kobayashi, N. *J. Org. Chem.* in press.
(14) (a) Sako, K.; Hirakawa, T.; Fujimoto, N.; Shinmyozu, T.; Inazu, T.; Horimoto, H. *Tetrahedron Lett.* **1988**, *29*, 6275. (b) Sako, K.; Shinmyozu, T.; Takemura, H.; Suenaga, M.; Inazu, T. *J. Org. Chem.* **1992**, *57*, 6536. (c) Shinmyozu, T.; Hirakawa, T.; Wen, G.; Osada, S.; Takemura, H.; Sako, K.; Rudzinski, J. M. *Liebigs Ann.* **1996**, 205. (d) Takemura, H.; Kariyazono, H.; Yasutake, M.; Kon, N.; Tani, K.; Sako, K.; Shinmyozu, T.; Inazu, T. *J. Org. Chem.* **1999**, *64*, 9077. (e) Satou, T.; Shinmyozu, T. *J. Chem. Soc., Perkin Trans. 2* **2002**, 393. (f) Sako, K.; Meno, T.; Takemura, H.; Shinmyozu, T.; Inazu, T. *Chem. Ber.* **1990**, *123*, 639. (g) Isaji, H.; Yasutake, M.; Takemura, H.; Sako, K.; Tatemitsu, H.; Inazu, T.; Shinmyozu, T. *Eur. J. Org. Chem.* **2001**, 2487.
(15) Hoogenboom, B. E.; Oldenziel, O. H.; van Leusen, A. M. *Org. Synth. Coll. Vol. VI*; John Wiley & Sons: London, **1988**, 987.