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# Construction of a Square-wave-shaped One-dimensional Polyrotaxane Using a Preorganized L-shaped Pseudorotaxane

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*Invited Paper*

# Construction of a Square-wave-shaped One-dimensional Polyrotaxane Using a Preorganized L-shaped Pseudorotaxane

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Dedicated to Professor Eiichi Kimura on the occasion of his retirement

*(Received 7 December 2001)*

**The construction of a square-wave-shaped one-dimensional polyrotaxane using a preorganized L-shaped [3]pseudorotaxane and metal ion is reported. A phenanthroline derivative having two *N*-(3-pyridylmethyl)-1,4-butanediammonium "arms" was synthesized as a preorganized L-shaped ligand. This L-shaped ligand easily forms a stable [3]pseudorotaxane incorporating cucurbituril (CB[6]). The reaction of the [3]pseudorotaxane with Ni(II) or Zn(II) ion produces a square-wave-shaped one-dimensional-polyrotaxane.**

*Keywords*: Coordination polymer; Cucurbituril; Metal ions; Polyrotaxane; Supramolecular Chemistry

## INTRODUCTION

Syntheses of interlocked structures [1–11] such as catenanes and rotaxanes are currently actively pursued in many laboratories in conjunction with the bottom-up strategies for the construction of nanoscale molecular machines [12–22]. For practical realization, such molecular machines should be organized into an array to behave in a coherent fashion. Therefore, we have explored organizing rotaxanes (or pseudorotaxanes) via self-assembly into polyrotaxanes with well-defined structures in the solid state [23–33]. Our synthetic strategy involves threading a cucurbituril (CB[6]) [34–36] "bead" with a linear "string" to form a stable pseudorotaxane, followed by linking the pseudorotaxanes with metal ions as "linkers" to organize into a one- or two-dimensional polyrotaxane. In principle, the overall topology and structure of the polyrotaxane can be controlled by the coordination number and geometry of the metal linker, and the structure of the pseudorotaxane.

We have recently extended this strategy to the construction of molecular necklaces in which a number of molecular beads are threaded on a large ring. In particular, we have synthesized a molecular necklace ([5]MN) [29], in which four molecular beads are threaded on a square framework, by utilizing a preorganized L-shaped pseudorotaxane (Scheme 1a). In this synthesis, two of the L-shaped pseudorotaxanes are joined by two metal ions in a face-to face fashion to form the molecular necklace. Instead of forming a discrete supermolecule with a square framework, however, such L-shaped pseudorotaxanes and metal ions would produce a square-wave-shaped one-dimensional polyrotaxanes if one end of the second L-shaped pseudorotaxane is linked to a third pseudorotaxane instead of the first (Scheme 1b). Here we report such an example: synthesis and

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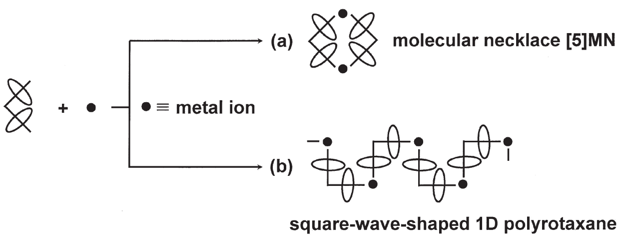


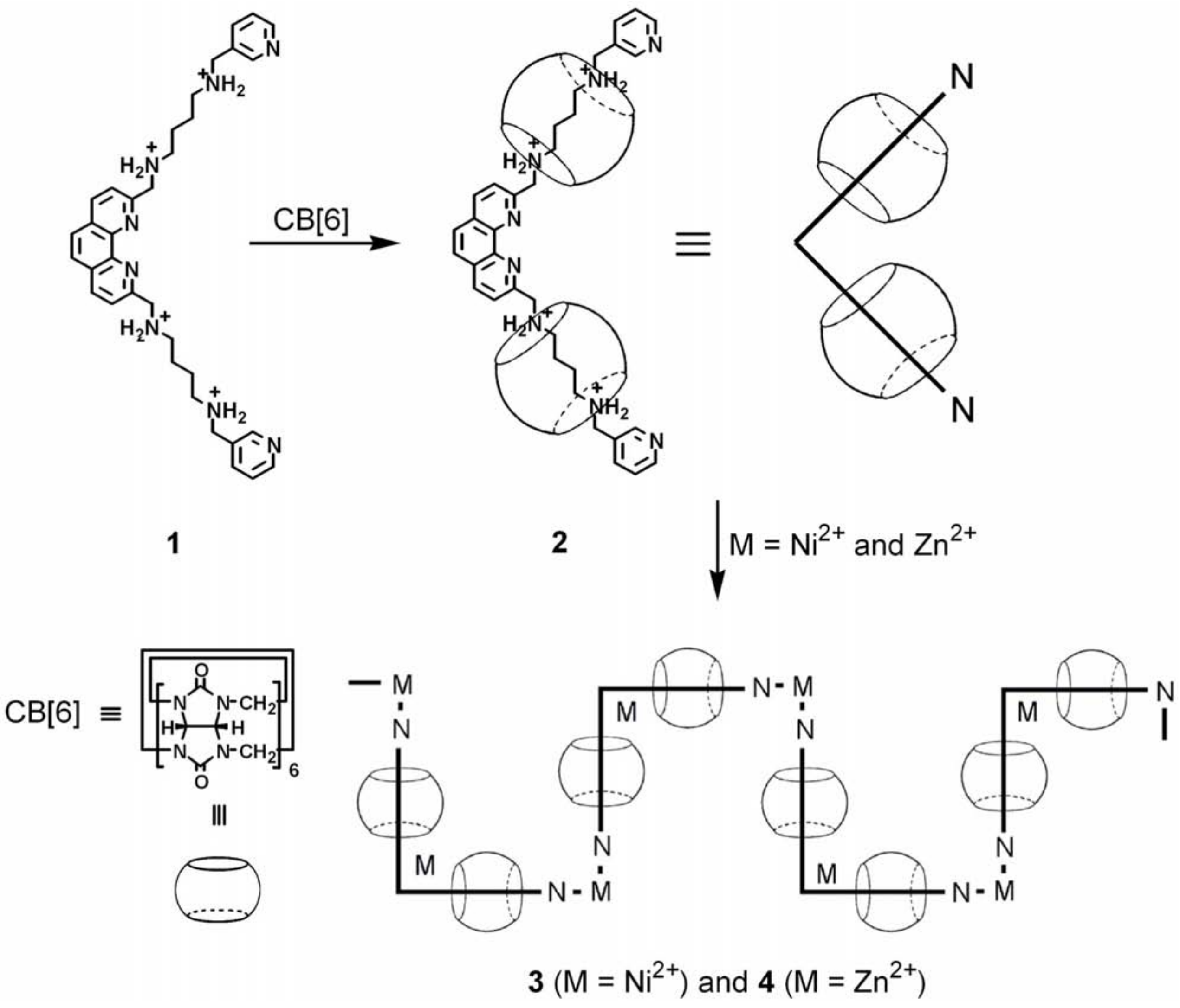
SCHEME 1 Synthetic scheme of (a) a molecular necklace [5]MN and (b) a square-wave-shaped one-dimensional polyrotaxane using a preorganized L-shaped pseudorotaxane.

X-ray crystal structure of novel square-wave-shaped one-dimensional polyrotaxanes using a preorganized L-shaped pseudorotaxane.

## RESULTS AND DISCUSSION

We designed the L-shaped "string" **1** that has a phenanthroline core and two 3-pyridylmethyl-1,4-butanediammonium "arms." The two arms of **1** not only form stable [3]pseudorotaxane with CB[6], but also bind metal ions using the donor atoms strategically placed at the terminals. Although CB[6] itself is sparingly soluble in water, the L-shaped [3]pseudorotaxane **2** readily dissolves in water because of their overall +4 charge. The pseudorotaxane can easily react with metal ions to organize it into a polyrotaxane under mild conditions. As shown in Scheme 2, slow reaction of $M(NO_3)_2$ ($M = Ni^{2+}$ and $Zn^{2+}$) with **2** at an ambient temperature produces one-dimensional polyrotaxanes **3** and **4** in solid state, respectively. Polyrotaxane **3** and **4** have been characterized by elemental analyses and X-ray crystallography.

X-ray crystal structures of **3** and **4**, which are isostructural, reveal that CB[6] "beads" are threaded on each "arm" of the L-shaped ligands, and the L-shaped [3]pseudorotaxanes are linked by metal ions to form one-dimensional coordination polymers. The asymmetric unit of **3** includes two $Ni^{2+}$ ions, a [3]pseudorotaxane, and eight coordinated



SCHEME 2 Synthesis of a square-wave-shaped one-dimensional polyrotaxane.

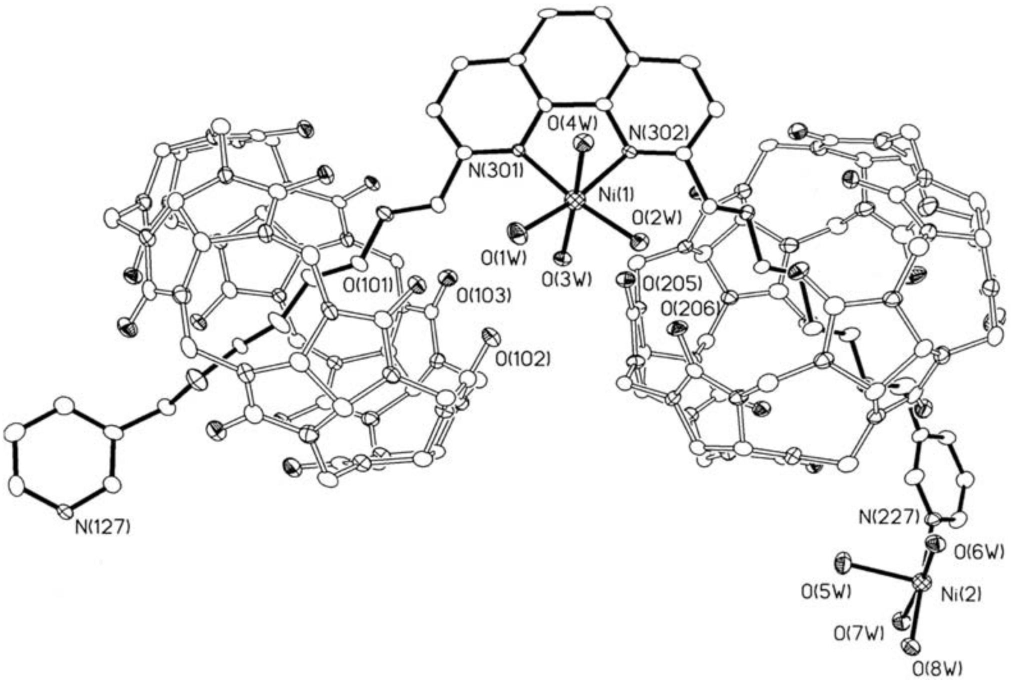


FIGURE 1 The asymmetric unit of **3**: nitrate ions and water molecules in the lattice are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)-N(301) 2.114(5), Ni(1)-N(302) 2.136(5); Ni(1)-O(1W) 2.078(5), Ni(1)-O(2W) 2.062(5) in equatorial position; Ni(1)-O(3W) 2.042(5), Ni(1)-O(4W) 2.076(5) in axial position; N(301)-Ni(1)-N(302) 78.58(19), O(3W)-Ni(1)-N(302) 99.90 (14); Ni(2)-N(227) 2.073(6), Ni(2)-N(127′) 2.092(6), Ni(2)-O(5W) 2.075(5), Ni(2)-O(6W) 2.073(5), Ni(2)-O(7W) 2.075(5), Ni(2)-O(8W) 2.066(5), O(5W)-Ni(2)-N(227) 90.55(17), N(127′)-Ni(2)-O(8W) 87.7(2).

water molecules (Fig. 1). One of the two unique nickel ions, Ni(1) is coordinated by the two phenanthroline nitrogen atoms and four water molecules in a distorted octahedral geometry. Ni(1) is displaced from the mean plane of the phenanthroline unit by ∼0.90Å− to avoid repulsion with the CB[6] beads threaded on the side arms leading to a distorted octahedral geometry. Hydrogen bonding interactions are observed between the water molecules bound to Ni(1) and the oxygen atoms of CB[6]: O(1W)Å−O(101) 2.671(7)Å−, O(2W)Å−O(206) 2.821(5)Å−, O(3W)Å−O(102) 2.765(7)Å−, O(3W)Å−O(205) 2.750(5)Å−. On the other hand, Ni(2), which behaves as a 90-degree angle connector, is coordinated by pyridyl groups of two different pseudorotaxanes and four water molecules in an octahedral geometry to produce an infinite one-dimensional polyrotaxane chain. The *cis* coordination of the two pyridine units to the metal center makes the polymer chain adopts a square-wave shape (Fig. 2). In the crystal of **3**, the coordination polymer chain runs along the [201] direction. As shown in Fig. 3, the square-wave-shaped one-dimensional polyrotaxane chains in **3** are stacked through $\pi-\pi$ interactions between the phenanthroline units, with a mean separation of 3.3Å.

This result is in sharp contrast to the molecular necklace [5]MN produced with a similar L-shaped pseudorotaxane (which has two 4-pyridylmethyl-1,4-butanediammonium arms instead of 3-pyridyl groups) and Cu(II) ion [29]. In the molecular necklace, the copper ions also behave as a 90-degree angle connector, but two of the copper ions work together to form a square framework for the molecular necklace. The question is then what makes the difference between the square-wave-shaped one-dimensional polyrotaxanes reported here and the previously reported molecular necklace [5]MN. Obviously, entropy favors the formation of the molecular necklace whereas crystal packing (intermolecular interaction) favors the formation of the one-dimensional polyrotaxane. However, the origin of the difference remains to be established.

In summary, we synthesized novel square-wave-shaped one-dimensional polyrotaxanes using a preorganized L-shaped ligand. The L-shaped pseudorotaxane and metal ions, which behave as a 90-degree angle connector, result in square-wave-shaped one-dimensional polyrotaxanes in the solid state. The present work along with our earlier work may provide insights into the construction of well-defined one-dimensional or two-dimensional arrays of rotaxane-based molecular machines that are useful for developing molecular electronic devices.

## EXPERIMENTAL SECTION

All reagents and solvents employed were commercially available high-grade purity materials, used as supplied without further purification. $^1$H-NMR

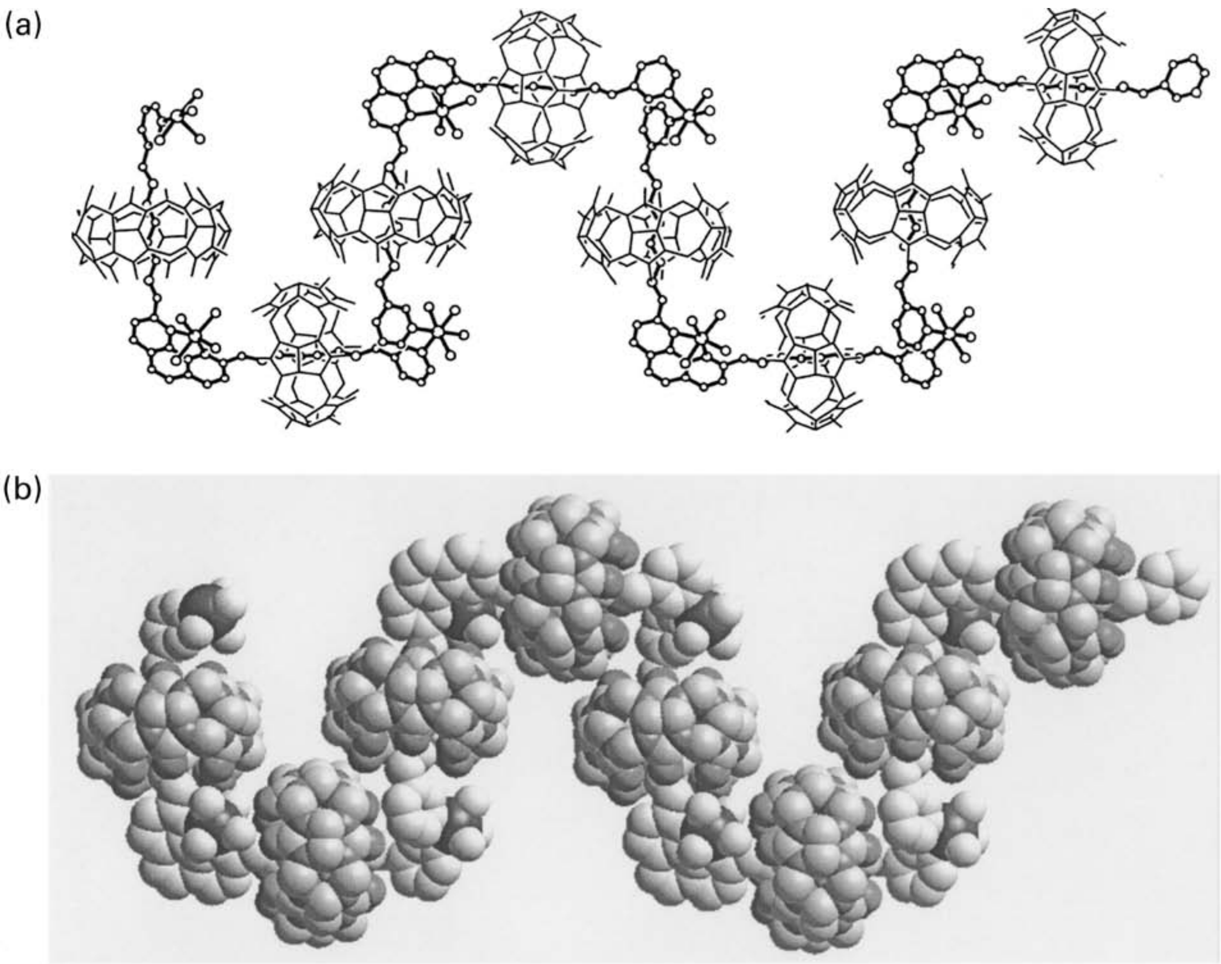


FIGURE 2 (a) X-ray crystal structure of square-wave-shaped one-dimensional polyrotaxane **3**, (b) a space-filling representation.

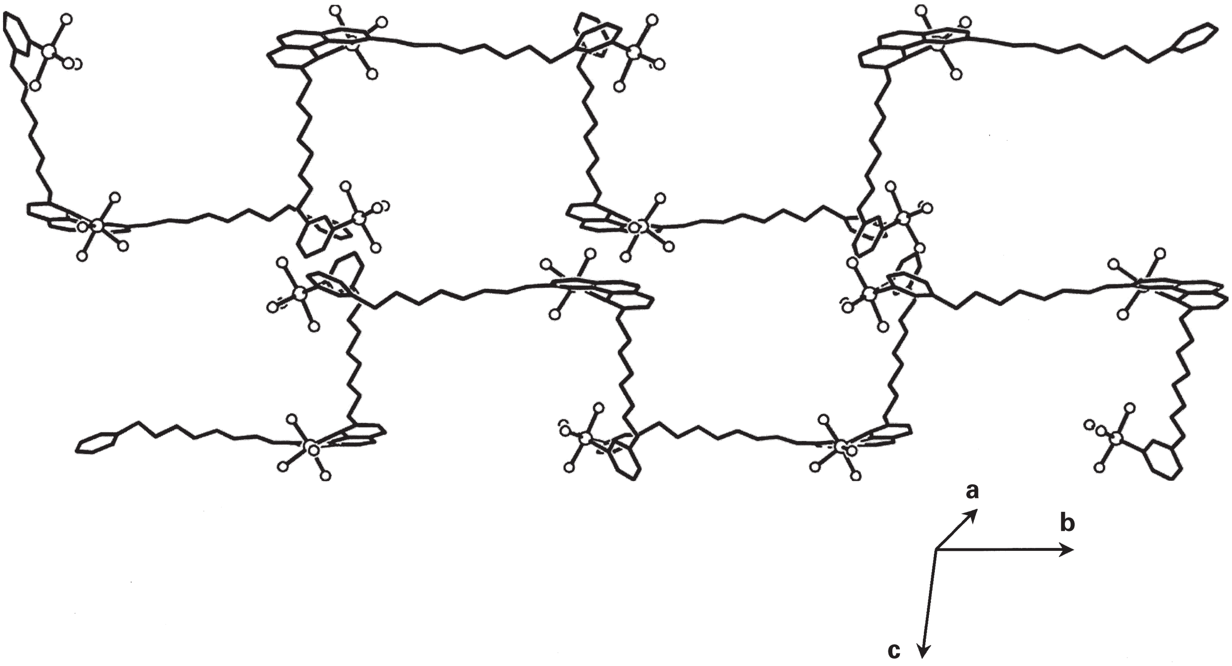


FIGURE 3 Packing view of **3**.

spectra were recorded on a Bruker AM-300 spectrometer. Samples for elemental analysis were dried under vacuum for several hours to overnight.

## Synthesis

**1**·4NO$_3$ and **2**·4NO$_3$ were synthesized using *N*-(3-pyridylmethyl)-1,4-diaminobutane trihydrobromide by the same methods as that have been reported earlier [29]. **1**·4NO$_3$: $^1$H NMR (300 MHz, D$_2$O) $\delta$ 1.92 (8H, s, br), 3.28 (4H, m), 3.37 (4H, m), 4.56 (4H, s), 8.01 (2H, **2**), 8.03(2H, s), 8.22(2H, m), 8.70 (2H, d), 8.79 (2H, d), 8.92 (2H, d), 8.99 (2H, s). **2**·4NO$_3$: $^1$H NMR (300 MHz, D$_2$O) $\delta$ 0.75 (8H, s, br), 2.56 (4H, s, br), 2.84 (4H, s, br), 4.51(24H, d, $J = 15.6$ Hz), 4.71 (4H, s), 5.01 (4H, s), 5.72–5.82 (48H, m), 8.14 (2H, m), 8.19 (2H, s), 8.69 (2H, d, $J = 8.40$ Hz), 8.83 (2H, d, $J = 8.04$ Hz), 8.94 (2H, d, $J = 5.67$ Hz), 9.00 (2H, d, $J = 8.13$ Hz), 9.28 (2H, s). Anal. Calcd for $C_{106}N_{60}O_{36}H_{118}\cdot 23H_2O$: C, 39.50; H, 5.12; N, 26.07. Found: C, 39.34; H, 4.85; N, 26.14.

**3**: A 3 mM solution of pseudorotaxane **2**·4NO$_3$ in H$_2$O was layered over a 0.3 M solution of Ni(NO$_3$)$_2$ in H$_2$O in a diffusion tube to produce pale green, plate-shape, X-ray quality crystals in two weeks (30 mg, 30%). Anal. Calcd for $C_{106}H_{118}N_{64}O_{48}\cdot Ni_2$ 30H$_2$O: C 33.94, H 4.89, N 23.90. Found: C 33.88, H 4.64, N 23.93.

**4**: Pale yellow, plate-shape, X-ray quality crystals of **4** were similarly obtained using Zn(NO$_3$)$_2$ (32 mg, 32%). Anal. Calcd for $C_{106}H_{118}N_{64}O_{48}Zn_2\cdot 31H_2O$: C 33.98, H 4.84, N 23.93. Found: C 33.94, H 4.89, N 23.90.

## X-ray Crystallographic Analysis

Single crystals coated with Paraton oil were transferred quickly under a cold nitrogen stream and mounted on a Siemens SMART diffractometer equipped with a graphite monochromated Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation source and a CCD detector. Intensity data were collected at 188 K. The data were processed with the program SAINT. The intensity data were corrected for Lorentz and polarization effects. Semi-empirical absorption correction based on multiple reflections was also applied. The structure was solved by a combination of Patterson methods (SHELXS-86) and successive difference Fourier techniques using Siemens SHELXTL-PC software package. All non-hydrogen atoms were refined anisotropically (SHELXL-93). Crystal data for **3**: $[Ni_2(C_{34}H_{46}N_8)\cdot(C_{36}H_{36}N_{24}O_{12})_2\cdot 8H_2O]\cdot(NO_3)_8\cdot 21H_2O$, $M_r = 3660.50$, monoclinic, $P2_1/c$, $a = 15.9121(3)$, $b = 32.7188(3)$, $c = 28.4046(8)$ Å$^3$, $\beta = 98.8307(2)°$, $V = 14612.8(4)_3$, $Z = 4$, $\rho_{calcd} = 1.664\,g\,cm^{-3}$, $\mu = 3.88\,cm^{-1}$. Final block-diagonal matrix least-squares refinement of $F^2$ with all 22,883 reflections and 2272 variables converged to $R1$ ($I > 2\sigma(I)$) = 0.085, $wR2$ (all data) = 0.231, and GOF = 1.06. Crystal data for **4**: $[Zn_2(C_{34}H_{46}N_8)\cdot(C_{36}H_{36}N_{24}O_{12})_2\cdot 8H_2O]\cdot(NO_3)_8\cdot 20.5H_2O$, $M_r = 3700.84$, monoclinic, $P2_1/c$, $a = 15.9944(3)$, $b = 32.8407(1)$, $c = 28.4560(4)$ Å, $\beta = 98.9190(10)°$, $V = 14677.3(3)$Å$^3$, $Z = 4$, $\rho_{calcd} = 1.665$ g cm$^{-3}$, $\mu = 4.55\,cm^{-1}$. Final block-diagonal matrix least-squares refinement on $F^2$ with all 23,106 reflections and 2272 variables converged to $R1$ ($I > 2\sigma(I)$) = 0.092, $wR2$ (all data) = 0.231, and GOF = 1.14. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-169744 (**3**) and CCDC-169745 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## *References*

[1] Lehn, J.-M. (1995) *Supramolecular Chemistry* (VCH, Weinhein).

[2] Leininger, S., Olenyuk, B. and Stang, P.J. (2000), *Chem. Rev.* **100**, 853.

[3] Balzani, V., Credi, A., Raymo, F.M. and Stoddart, J.F. (2000), *Angew. Chem. Int. Ed. Engl.* **39**, 3349.

[4] Swiegers, G.F. and Malefetse, J. (2000), *Chem. Rev.* **100**, 3483.

[5] Nepogodiev, S.A. and Stoddart, J.F. (1998), *Chem. Rev.* **98**, 1959.

[6] Amabilino, D.B. and Stoddart, J.F. (1995), *Chem. Rev.* **95**, 2725.

[7] Philip, D. and Stoddart, J.F. (1996), *Angew. Chem. Int. Ed. Engl.* **35**, 1154.

[8] Jäger, R. and Vogtle, F. (1997), *Angew. Chem. Int. Ed. Engl.* **36**, 930.

[9] Vögtle, F., Dünnwald, T. and Schmidt, T. (1996), *Acc. Chem. Res.* **29**, 451.

[10] Fujita, M. (1999), *Acc. Chem. Res.* **32**, 53.

[11] Sauvage, J.-P. (1998), *Acc. Chem. Res.* **31**, 611.

[12] Colloer, C.P., Wong, E.W., Belohradsky, M., Raymo, F.M., Stoddart, J.F., Kuekes, P.J., Williams, R.S. and Heath, J.R. (1999), *Science* **285**, 391.

[13] Swager, T.M. (1998), *Acc. Chem. Res.* **31**, 201.

[14] Pease, A.R., Jeppesen, J.O., Stoddart, J.F., Luo, Y., Collier, C.P. and Heath, J.R. (2001), *Acc. Chem. Res.* **34**, 433.

[15] Ballardini, R., Balzani, V., Credi, A.M., Gandolfi, T. and Venturi, M. (2001), *Acc. Chem. Res.* **34**, 445.

[16] Harada, A. (2001), *Acc. Chem. Res.* **34**, 465.

[17] Schalley, C.A., Beizai, K. and Vögtle, F. (2001), *Acc. Chem. Res.* **34**, 465.

[18] Collin, J.-P., Buchecker, C.D., Gavina, P., Molero, M.C.J. and Sauvage, J.-P. (2001), *Acc. Chem. Res.* **34**, 477.

[19] Amendola, V., Fabbrizzi, L., Mangano, C. and Pallavicini, P. (2001), *Acc. Chem. Res.* **34**, 488.

[20] Shinkai, S., Ikeda, M., Sugasaki, A. and Takeuchi, M. (2001), *Acc. Chem. Res.* **34**, 494.

[21] Feringa, B.L. (2001), *Acc. Chem. Res.* **34**, 504.

[22] Kelly, T.R. (2001), *Acc. Chem. Res.* **34**, 514.

[23] Jeon, Y.-M., Whang, D., Kim, J. and Kim, K. (1996), *Chem. Lett.*, 503.

[24] Whang, D., Jeon, Y.-M., Heo, J. and Kim, K.J. (1996), *Am. Chem. Soc.* **118**, 11333.

[25] Whang, D. and Kim, K. (1997), *J. Am. Chem. Soc.* **119**, 451.

[26] Whang, D., Heo, J., Kim, C.-A. and Kim, K. (1997), *J. Chem. Soc. Commun.*, 2361.

[27] Lee, E., Heo, J. and Kim, K. (2000), *Angew. Chem. Int. Ed.* **39**, 2699.

[28] Whang, D., Park, K.-M., Heo, J. and Kim, K. (1998), *J. Am. Chem. Soc.* **120**, 4899.

[29] Roh, S.-G., Park, K.-M., Park, G.-J., Sakamoto, S., Yamaguchi, K. and Kim, K. (1999), *Angew. Chem. Int. Ed.* **38**, 638.

[30] Lee, E., Kim, J., Heo, J., Whang, D. and Kim, K. (2001), *Angew. Chem. Int. Ed.* **40**, 399.

[31] Lee, J.W., Ko, Y.H., Park, S.-H., Yamaguchi, K. and Kim, K. (2001), *Angew. Chem. Int. Ed.* **40**, 746.

[32] Jun, S.I., Lee, J.W., Sakamoto, S., Yamaguchi, K. and Kim, K. (2000), *Tetrahedron Lett.* **41**, 471.

[33] Lee, J.W., Kim, K. and Kim, K. (2001), *Chem. Commun.*, 1042.

[34] Mock, W.L. (1995), *Top. Curr. Chem.* **175**, 1.

[35] Mock, W.L. (1996) In: Vögtle, F., ed, *Comprehensive Supramolecular Chemistry* (Pergamon, Oxford) Vol. 2, p 477.

[36] Kim, J., Jung, I.S., Kim, S.Y., Lee, E., Kang, J.-K., Sakamoto, S., Yamaguchi, K. and Kim, K. (2000), *J. Am. Chem. Soc.* **122**, 540.