

Assembly of Hydrogen-Bonded Organic Layers with Macrocyclic Complexes Acting as Pillars

Myunghyun Paik Suh,^{*,[a]} Kil Sik Min,^[a] Jung Woo Ko,^[a] and Hye Jin Choi^[a]

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Novel supramolecular networks of 2D $\{[\text{Ni}(\text{cyclam})][\text{C}_6\text{H}_9(\text{COOH})_2(\text{COO})]_2\}_n$ (**1**) and 3D $\{[\text{Ni}(\text{cyclam})][\text{C}_6\text{H}_3(\text{OH})_2(\text{COO})]_2\}_n$ (**2**) have been constructed by the self-assembly of $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ with *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (H_3CTC) and 3,5-dihydroxybenzoic acid (HDHB), respectively, in py/MeCN/ H_2O . In the crystal structure of **1**, each nickel(II) macrocyclic complex binds two H_2CTC^- ions at the axial sites. The coordinated H_2CTC^- ions form hydrogen bonds with one another, which results in organic bilayers having macrocyclic complexes as pillars. In the crystal struc-

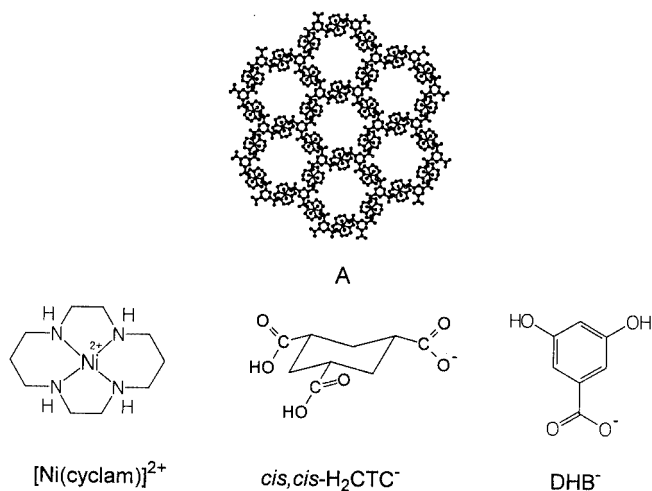
ture of **2**, each nickel(II) macrocyclic complex binds two DHB^- ions in the *trans* position. Two free hydroxyl groups and one carbonyl oxygen atom of the coordinated DHB^- ion are extensively hydrogen-bonded with the DHB^- ligand of the neighboring complexes, which results in a 3D network where 2D organic layers are linked by the macrocyclic complexes acting as pillars.

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Introduction

Supramolecular solids with various network topologies and with interesting properties have been prepared by the self-assembly of transition metal ions and organic building blocks.^[1,2] In the self-assembly of supramolecules, hydrogen bonding,^[3] metal-ligand coordination,^[4] and π - π interactions^[5] are involved in multidimensional intermolecular interactions. In particular, directional hydrogen-bonding interactions are important for materials design^[6] and molecular recognition.^[7,8] It has been demonstrated that extensive hydrogen-bonding interactions in organic compounds result in remarkably robust three-dimensional networks.^[9] In addition, frameworks with different topologies can be constructed by changing the hydrogen-bonding mode.^[10,11] Macrocyclic complexes have been rarely employed as metal building blocks in the self-assembly of supramolecular networks.^[12,13] Recently, a molecular floral lace with 1D channels, $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]_3[\text{C}_6\text{H}_3(\text{COO})_3]_2 \cdot 24\text{H}_2\text{O}$ (**A**), was assembled by the extensive hydrogen-bonding interactions between the coordinated water molecules of $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$ and 1,3,5-benzenetricarboxylate.^[12]

Here we report 2D $\{[\text{Ni}(\text{cyclam})][\text{C}_6\text{H}_9(\text{COOH})_2(\text{COO})]_2\}_n$ (**1**) and 3D $\{[\text{Ni}(\text{cyclam})][\text{C}_6\text{H}_3(\text{OH})_2(\text{COO})]_2\}_n$ (**2**) supramolecular networks, which are assembled from $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ with *cis,cis*-1,3,5-cyclohexanetricar-



boxylic acid (H_3CTC) and 3,5-dihydroxybenzoic acid (HDHB), respectively, in the presence of pyridine. Multidimensional networks **1** and **2** are generated by the extensive hydrogen-bonding interactions between the organic building blocks, giving rise to 2D layers with the macrocyclic complexes acting as pillars connecting the organic layers. To the best of our knowledge, this is the first example where macrocyclic complexes are involved as pillars linking the organic layers in the supramolecular networks. This synthetic strategy can be applied to construct hybrid materials that consist of alternately packed organic-inorganic layers.

Results and Discussion

Self-Assembly and Properties of 2D and 3D Networks

Our synthetic strategy to build multidimensional networks was based on the hydrogen-bonding interactions be-

^[a] School of Chemistry and Molecular Engineering, and Center for Molecular Catalysis, Seoul National University, Seoul 151-747, Republic of Korea
Fax: (internat.) +82-2/886-8516
E-mail: mpsuh@snu.ac.kr

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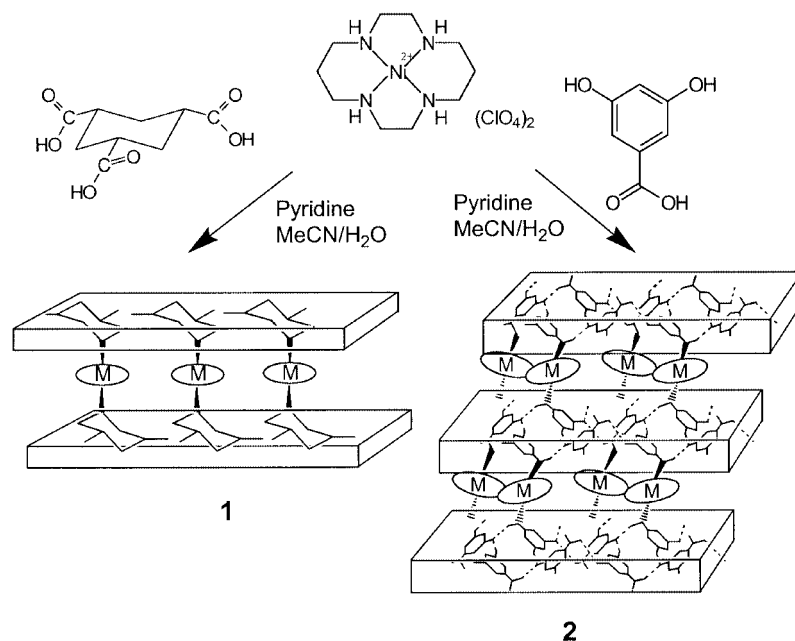
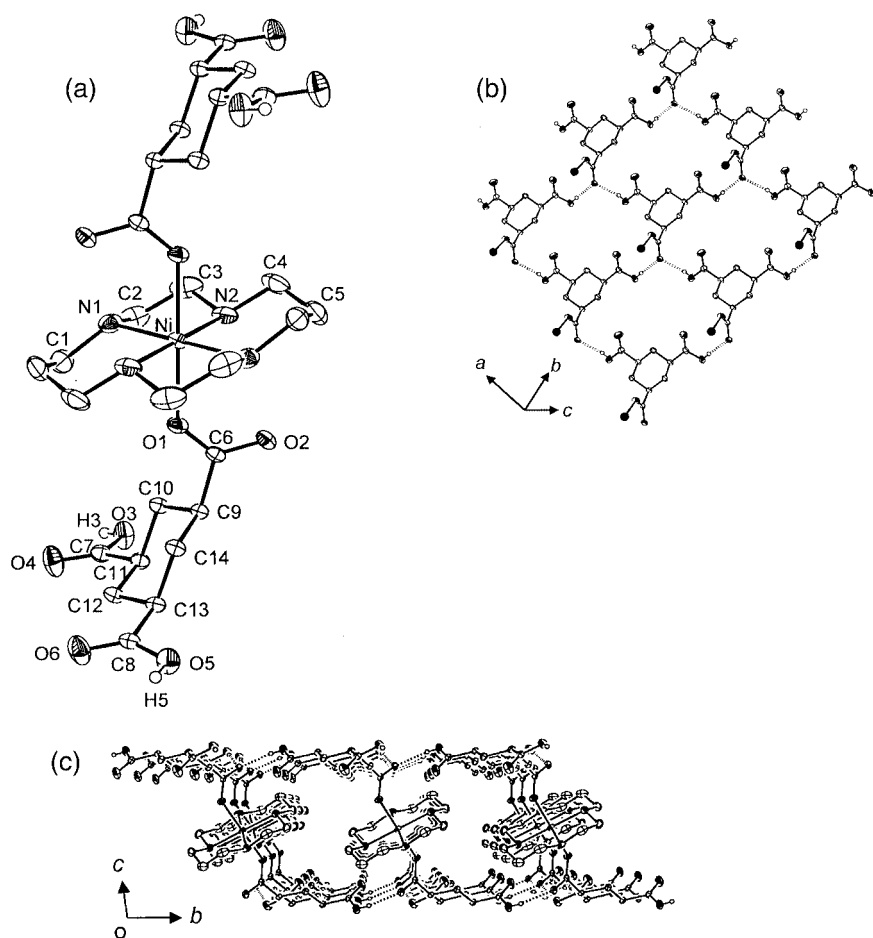
Scheme 1. Synthetic strategy for **1** and **2**

Figure 1. (a) An ORTEP view of **1** with atomic numbering scheme; the atoms are represented by 40% probability thermal ellipsoids; (b) the 2D organic layer, showing 26-membered supramolecular synthons constructed by the hydrogen bonding interactions between the coordinated H_2CTC^- ions; metal ions are indicated as filled black circles and intermolecular hydrogen bonds are indicated as dotted lines; (c) a view from the bc plane, showing the bilayer network where macrocyclic complexes act as pillars

tween organic ligands, which led to 2D organic layers with the macrocyclic complexes linking the organic layers as pillars. For this, [Ni(cyclam)](ClO₄)₂^[14] and the carboxylate anions derived from *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (H₃CTC) and 3,5-dihydroxybenzoic acid (HDHB) were used as the building blocks (Scheme 1).

When [Ni(cyclam)](ClO₄)₂ was reacted in MeCN/H₂O (1:1 v/v) with *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (H₃CTC) in the presence of pyridine, only one proton of H₃CTC was removed and [Ni(cyclam)]²⁺ was coordinated by two H₂CTC[−] anions to form {[Ni(cyclam)][C₆H₉(COOH)₂(COO)]₂}_n (**1**). When [Ni(cyclam)](ClO₄)₂ was reacted in MeCN/H₂O (1:1 v/v) with 3,5-dihydroxybenzoic acid (HDHB) in the presence of pyridine, the carboxylic acid group of HDHB was deprotonated and [Ni(cyclam)]²⁺ was coordinated with two DHB[−] anions to form {[Ni(cyclam)][C₆H₃(OH)₂(COO)]₂}_n (**2**).

The supramolecular compounds **1** and **2** are pink and air-stable. They are insoluble in all solvents except water. In water, they are dissociated into the building blocks, as evidenced by the UV/Vis spectra, which exhibit the characteristic chromophore ($\lambda_{\text{max}} = 445 \text{ nm}$) of the starting material [Ni(cyclam)]²⁺. The diffuse reflectance spectrum measured for a powdered sample of **1** shows maximum absorptions at 332, 505, and 648 nm and that of **2** at 300, 511, and 661 nm, which correspond to the chromophores of nickel(II) ions coordinated by N₄O₂ donors.^[15] The TGA and DSC traces of **1** and **2** (Figures S1 and S2) show that decomposition starts at 240 and 220 °C, respectively.

X-ray Crystal Structure of 1

An ORTEP^[16] drawing of **1** is shown in Figure 1a. Table 1 shows selected bond lengths and angles. In the crystal structure of **1**, the nickel(II) ion of the macrocyclic complex [Ni(cyclam)]²⁺ is coordinated to two carboxylate oxygen atoms of H₂CTC[−] ions at the axial sites (Figure 1a). The complex has an inversion center at the nickel(II) ion. The average Ni–N bond length is 2.042(1) Å and the average Ni–O bond length is 2.171(1) Å, similar to those of open-framework A.^[12] The coordinated H₂CTC[−] ligands are linked to one another by the extensive hydrogen-bonding interactions. Each carbonyl oxygen atom of the coordinated carboxylate group of H₂CTC[−] behaves as a hydrogen acceptor to form bifurcated hydrogen bonds with two carboxylic acid groups belonging to two different H₂CTC[−] ions of the adjacent macrocyclic complexes [O2...O3'(x − 1, y, z): 2.701(2) Å; O2...H3'–O3': 172.73°; O2...O5''(x, y − 1, z): 2.700(2) Å; O2...H5''–O5'': 172.74°], and two free carboxylic acid groups of the H₂CTC[−] ligand behave as hydrogen donors and form hydrogen bonds with the carbonyl oxygen atoms of the H₂CTC[−] ligands belonging to two different adjacent complexes. The extensive hydrogen-bonding interactions between H₂CTC[−] ligands construct 26-membered supramolecular synthons that propagate infinitely parallel to the crystallographic *ab* plane to give rise to a 2D organic network (Figure 1b). Due to the hydrogen-bonding interactions, the free C=O bond length of H₂CTC[−] [C6–O2, 1.266(2) Å] is longer than that of the

Table 1. Selected bond lengths (Å) and angles (°) for **1**^[a]

Ni1–N1	2.042(2)	C1–C5'	1.501(5)
Ni1–N2	2.042(2)	C2–C3	1.498(4)
Ni1–O1	2.171(1)	C4–C5	1.498(5)
O1–C6	1.241(2)	C6–C9	1.526(2)
O2–C6	1.266(2)	C7–C11	1.507(3)
O3–C7	1.314(3)	C8–C13	1.504(3)
O4–C7	1.200(3)	C9–C10	1.527(2)
O5–C8	1.317(3)	C9–C14	1.528(2)
O6–C8	1.199(3)	C10–C11	1.530(2)
N1–C2	1.458(3)	C11–C12	1.520(3)
N1–C1	1.471(3)	C12–C13	1.518(3)
N2–C3	1.458(3)	C13–C14	1.530(2)
N2–C4	1.475(3)		
N1–Ni1–N2	85.82(9)	O4–C7–O3	122.43(19)
N1–Ni1–O1	89.44(7)	O4–C7–C11	124.64(18)
N2–Ni1–O1	90.72(7)	O3–C7–C11	112.86(17)
O1'–Ni1–O1	180.00(7)	O6–C8–O5	122.27(19)
C6–O1–Ni1	132.12(12)	O6–C8–C13	124.74(18)
C2–N1–C1	114.1(2)	O5–C8–C13	112.92(17)
C2–N1–Ni1	105.27(15)	C6–C9–C10	110.17(14)
C1–N1–Ni1	116.57(16)	C6–C9–C14	110.29(14)
C3–N2–C4	114.1(2)	C10–C9–C14	111.21(15)
C3–N2–Ni1	105.33(15)	C9–C10–C11	111.28(14)
C4–N2–Ni1	116.56(16)	C7–C11–C12	110.50(15)
N1–C1–C5'	113.1(2)	C7–C11–C101	10.13(15)
N1–C2–C3	108.9(2)	C12–C11–C10	110.15(15)
N2–C3–C2	108.8(2)	C13–C12–C11	110.59(15)
N2–C4–C5	113.0(2)	C8–C13–C12	110.61(15)
C4–C5–C1'	115.4(2)	C8–C13–C14	110.46(15)
O1–C6–O2	124.30(17)	C12–C13–C14	109.89(15)
O1–C6–C9	117.66(16)	C9–C14–C13	111.58(15)
O2–C6–C9	118.04(16)		

^[a] Symmetry transformations used to generate equivalent atoms: ' : −x, −y, −z.

coordinated C–O bond length [C6–O1, 1.241(2) Å]. Since both of the H₂CTC[−] ions coordinating a nickel(II) macrocyclic complex are involved in the formation of two different 2D organic layers, the structure becomes a bilayer containing nickel(II) macrocycles acting as pillars (Figure 1c). The interlayer distance within the bilayer is 5.692(4) Å and the shortest distance between two adjacent bilayers (C...O) is 3.399(3) Å.

X-ray Crystal Structure of 2

An ORTEP^[16] drawing of **2** is shown in Figure 2a. Table 2 shows selected bond lengths and angles. In the crystal structure of **2**, the nickel(II) ion of the macrocyclic complex binds two carboxylate oxygen atoms of DHB[−] ions at the axial sites (Figure 2a). The complex has an inversion center at the nickel(II) ion. The average Ni–N and Ni–O bond lengths are 2.065(1) and 2.130(1) Å, respectively, which are similar to those of **1**. The aromatic ring of the DHB[−] ion is tilted with respect to the square coordination plane of the macrocycle [dihedral angle = 51.3(1)°]. The DHB[−] ligand is not planar since the dihedral angle between the carboxylate group and the aromatic ring of DHB[−] ion is 29.9(3)°. Within the molecule, there are hydrogen-bonding interactions between the carbonyl oxygen atoms of the carboxylate ions and the secondary amines of the macrocy-

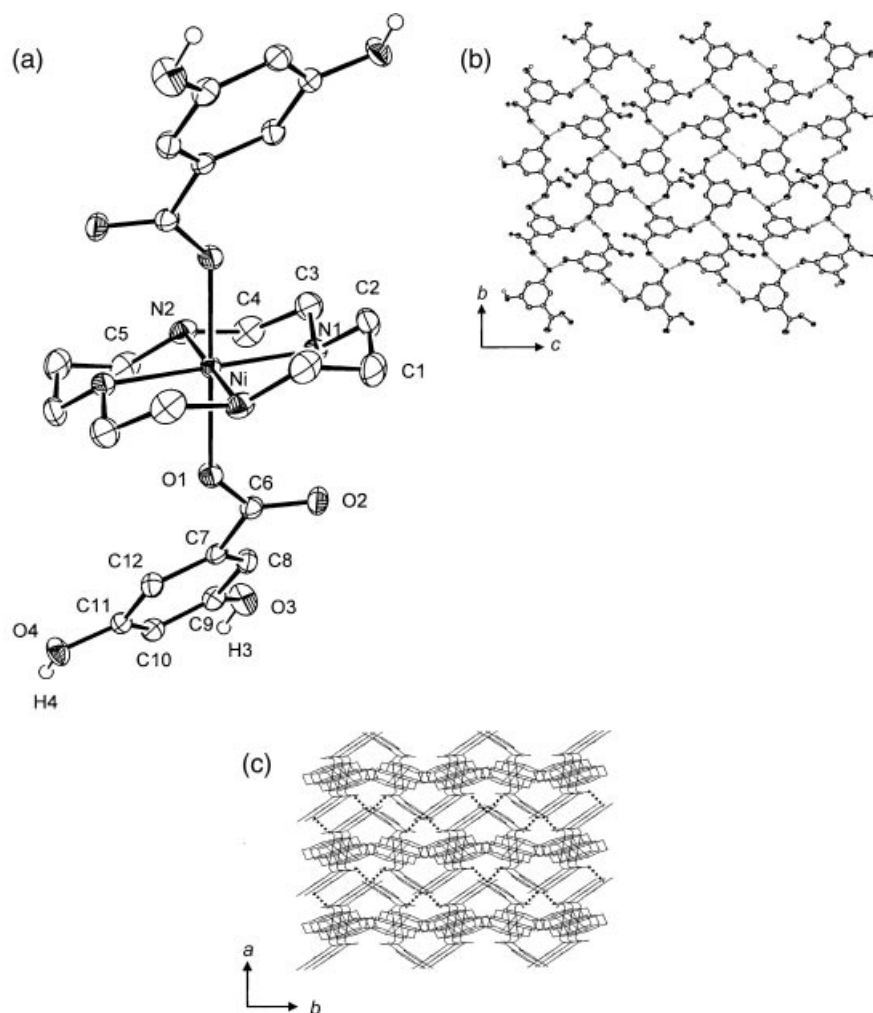
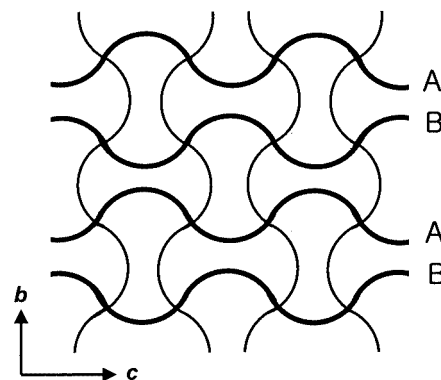


Figure 2. (a) An ORTEP view of **2** with atomic numbering scheme; the atoms are represented by 40% probability thermal ellipsoids; intramolecular hydrogen bonds are indicated as dotted lines; (b) a 2D organic layer constructed by the hydrogen-bonding interactions between the coordinated DHB[−] ligands; (c) a view of the 3D network on the *ab* plane, showing how the thick 2D organic layers are linked by the macrocyclic complexes acting as pillars, interlayer hydrogen bonds are indicated as ····

cle to form six-membered rings [O2···N1: 2.980(3) Å; O2···H1–N1: 162°]. The six-coordinate nickel(II) macrocyclic complexes are linked together by extensive hydrogen-bonding interactions between the DHB[−] ligands. Each DHB[−] ion coordinating the metal above the plane forms hydrogen bonds with two neighboring DHB[−] ligands, via hydroxyl groups [O3···O4(#1) (#1: *x*, *−y* + 0.5, *z* + 0.5): 2.763(2) Å; O3–H3(#1)···O4(#1): 164°], to build a 1D chain that extends along the crystallographic *c* axis, undulating in the *b* and *a* directions (Figure 2b; A in Scheme 2). Similarly, each DHB[−] ligand coordinating a metal below the macrocyclic coordination plane also forms hydrogen bonds with two adjacent DHB[−] ligands to construct another undulating 1D chain that also extends along the *c* direction (B in Scheme 2). These two kinds of chains are alternately aligned toward the *b* direction, and they are connected to one another by the hydrogen-bonding interactions via the free carbonyl oxygen atom of the coordinated carboxylate group of DHB[−] belonging to one chain and the hydroxyl group of DHB[−] belong to the other chain [O2···O4(#2) (#2 = *−x* − 1, *y* + 0.5, *−z* + 0.5): 2.610(2)

Å; O2···H4(#2)–O4(#2): 175°]. There are π – π interactions between the phenyl rings of DHB[−] belonging to the adjacent chains [centroid···centroid distance: 6.032 Å; closest C···C distance: 3.917(4) Å]. Since the interchain hydrogen-bonding interactions extend along the *b* direction and undulate in the *a* direction, the DHB[−] ligands construct a



Scheme 2. Schematic drawing of formation of 2D organic layer in **2**

Table 2. Selected bond lengths (Å) and angles (°) for **2**^[a]

Ni–N1	2.065(2)	C1–C5'	1.515(4)
Ni–N2	2.065(2)	C1–C2	1.517(4)
Ni–O1	2.130(2)	C3–C4	1.513(4)
N1–C3	1.465(3)	C6–C7	1.498(3)
N1–C2	1.478(3)	C7–C12	1.389(3)
N2–C5	1.469(3)	C7–C8	1.393(3)
N2–C4	1.482(3)	C8–C9	1.386(3)
O1–C6	1.258(3)	C9–C10	1.388(3)
O2–C6	1.258(3)	C10–C11	1.387(3)
O3–C9	1.360(3)	C11–C12	1.392(3)
O4–C11	1.368(3)		
N2–Ni–N1	85.23(8)	O1–C6–O2	124.4(2)
N2–Ni–O1	92.00(7)	O1–C6–C7	116.47(17)
N1–Ni–O1	92.92(7)	O2–C6–C7	119.05(19)
C3–N1–C2	113.62(19)	C12–C7–C8	120.12(19)
C3–N1–Ni	106.20(14)	C12–C7–C6	119.92(18)
C2–N1–Ni	116.08(14)	C8–C7–C6	119.83(19)
C5–N2–C4	114.4(2)	C9–C8–C7	119.8(2)
C5–N2–Ni	115.88(16)	O3–C9–C8	116.7(2)
C4–N2–Ni	106.24(15)	O3–C9–C10	122.55(19)
C6–O1–Ni	132.68(14)	C8–C9–C10	120.73(19)
C5'–C1–C2	115.8(2)	C11–C10–C9	119.02(19)
N1–C2–C1	112.45(19)	O4–C11–C10	122.09(19)
N1–C3–C4	109.08(19)	O4–C11–C12	116.91(19)
N2–C4–C3	108.9(2)	C10–C11–C12	120.99(19)
N2–C5–C1'	111.77(19)	C7–C12–C11	119.33(19)

^[a] Symmetry transformations used to generate equivalent atoms: ' : $-x, -y, -z$.

thick 2D organic layer (Figure 2b and 2c). The thickness of the organic layer is 4.872(3) Å. These thick 2D organic layers are linked by the macrocyclic complexes located on a plane parallel to the *bc* plane, and thus the whole structure can be viewed as a 3D network where macrocyclic complexes act as pillars (Figure 2c).

Conclusion

A 2D bilayered framework (**1**) and a 3D supramolecular network (**2**), where macrocyclic complexes behave as pillars linking 2D organic layers, have been prepared by the self-assembly of the nickel(II) macrocyclic complex [Ni(cyclam)]²⁺ with *cis,cis*-1,3,5-cyclohexanetricarboxylate (H₂CTC[−]) and 3,5-dihydroxybenzoate (DHB[−]), respectively. The multi-dimensional networks are constructed by the extensive hydrogen-bonding interactions between the organic ligands coordinating the nickel(II) ions. The synthetic strategy can be applied to construct hybrid materials that consist of organic layers and layers of transition metal complexes packed alternately.

Experimental Section

General Remarks: All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. [Ni(cyclam)](ClO₄)₂ was prepared according to the literature procedures previously reported.^[14] Infrared spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrophotometer. Elemental analy-

ses were performed by the analytical laboratory of Seoul National University. UV/Vis diffuse reflectance spectra were recorded with a Cary 300 Bio UV/Vis spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a scan rate of 5 °C/min using a DuPont TGA 2050 and a DuPont DSC 2100 TA instrument, respectively.

Safety Note: Perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution, although we have experienced no problem with the compounds reported in this work.

{[Ni(cyclam)][C₆H₉(COOH)₂(COO)]₂}_n (1**):** An MeCN solution (6 mL) of *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (H₃CTC; 0.14 g, 0.76 mmol) mixed with pyridine (1 mL) was added dropwise to an MeCN/H₂O (1:1 v/v, 12 mL) solution of [Ni(cyclam)](ClO₄)₂ (0.17 g, 0.38 mmol). The yellow color of the nickel(II) solution turned to pale pink. The solution was allowed to stand at room temperature until pale pink crystals of {[Ni(cyclam)][C₆H₉(COOH)₂(COO)]₂}_n formed, which were filtered, washed with MeCN/H₂O (1:1 v/v), and dried in air. There is no other form of aggregation present in the solution. Yield: 0.20 g (77%). C₂₈H₄₆N₄NiO₁₂: calcd. C 48.78, H 6.73, N 8.13; found C 48.60, H 6.55, N 8.50. FT-IR (Nujol mull): $\tilde{\nu}$ = 3300 (s), 3123 (s), 3084 (s), 1721 (s), 1548 (s), 1251 (s), 1177 (s), 954 (s), 870 (s), 730 (s), 649 (s) cm^{−1}. UV/Vis (diffuse reflectance spectrum): λ_{max} = 332, 505, 648 nm.

{[Ni(cyclam)][C₆H₃(OH)₂(COO)]₂}_n (2**):** An MeCN solution (6 mL) of 3,5-dihydroxybenzoic acid (0.14 g, 0.88 mmol) and pyridine (1 mL) was added dropwise to an MeCN/H₂O (1:1 v/v, 12 mL) solution of [Ni(cyclam)](ClO₄)₂ (0.20 g, 0.44 mmol). The yellow color of the nickel(II) solution turned to pale pink. The solution was allowed to stand at room temperature until pale pink crystals of {[Ni(cyclam)][C₆H₃(OH)₂(COO)]₂}_n formed, which were filtered off, washed with MeCN/H₂O (1:1 v/v), and dried in air. There is no other form of aggregation present in the solution. Yield: 0.19 g (75%). C₂₄H₃₄N₄NiO₈: calcd. C 51.00, H 6.06, N 9.91; found C 50.27, H 6.17, N 9.98. FT-IR (Nujol mull): $\tilde{\nu}$ = 3306 (s), 3200 (s), 3062 (s), 2554 (s, br), 1558 (s), 1393 (s), 1284 (s), 1156 (s), 1025 (s), 958 (s), 792 (s), 689 (s) cm^{−1}. UV/Vis (diffuse reflectance spectrum): λ_{max} = 248, 300, 511, 661 nm.

X-ray Crystallographic Study: Single crystals of **1** and **2** were mounted on an Enraf–Nonius CAD4 diffractometer. The unit-cell parameters were determined from 25 machine-centered reflections with 22° < 2θ < 28° for **1** and 22° < 2θ < 27° for **2**. Intensities were collected with graphite-monochromated Mo-*K*_α radiation (λ = 0.71069 Å), using the ω-2θ scan. Three standard reflections were measured every 2 h for the orientation and intensity control; no significant intensity decay was observed. The data were corrected for Lorentz and polarization effects. No absorption correction was made. For **1**, among 2618 reflections measured in the range 3.78 < 2θ < 49.88, 2552 were assumed to be observed [*F* > 4σ(*F*)]. For **2**, among 2193 reflections measured in the range 4.80 < 2θ < 49.94, 1842 were assumed to be observed [*F* > 4σ(*F*)]. The crystal structures were solved by direct methods^[17] and refined by full-matrix least-squares methods using the SHELXL-97 computer program.^[18] For **1** and **2**, the positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The carboxylic acid protons and hydroxyl protons were located from the difference Fourier maps and refined with isotropic thermal parameters. The remaining hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values of 1.2-times those of the bonded atoms. ORTEP drawings were made

Table 3. Crystallographic data for **1** and **2**

	1	2
Formula	C ₂₈ H ₄₆ N ₄ NiO ₁₂	C ₂₄ H ₃₄ N ₄ NiO ₈
M	689.40	565.26
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	8.349(2)	8.563(1)
<i>b</i> (Å)	8.361(3)	13.079(2)
<i>c</i> (Å)	10.803(4)	11.283(3)
α (°)	85.75(3)	90
β (°)	85.82(2)	98.74(1)
γ (°)	88.23(2)	90
<i>V</i> (Å ³)	749.8(4)	1249.0(4)
<i>Z</i>	1	2
μ (mm ⁻¹)	0.719	0.834
<i>T</i> (K)	293(2)	293(2)
Total measured reflections	2857	2372
Total unique reflections	2618 (<i>R</i> _{int} = 0.0069)	2193 (<i>R</i> _{int} = 0.0127)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2552	1842
<i>R</i> 1 (all data) ^[a]	0.0348	0.0412
<i>wR</i> 2 (all data) ^[b]	0.0931	0.0860

^[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^[b] $wR2 = [\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|)^4]]^{1/2}$.

with ORTEP-3 for Windows.^[16] The crystallographic data of **1** and **2** are summarized in Table 3.

CCDC-193023 (**1**) and -193024 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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- [1] ^[1a] K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **2000**, *122*, 6834. ^[1b] M. Eddaoudi, D. B. Li, H. Moler, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319. ^[1c] M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376. ^[1d] T. L. Hennigart, D. C. Macquarrie, P. Losier, R. D. Rogers, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 972.
- [2] ^[2a] P. J. Hagrman, D. Hagrman, J. Zubietta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2639. ^[2b] Y.-H. Kiang, G. B. Gardner, S. Lee, Z. Xu, *J. Am. Chem. Soc.* **2000**, *122*, 6871. ^[2c] E. Corradi, S. V. Meille, M. T. Messina, P. Metrangolo, G. Resnati, *Angew. Chem. Int. Ed.* **2000**, *39*, 1782. ^[2d] H. Gudbjartson, K. Biradha, K. M. Poirier, M. J. Zaworotko, *J. Am. Chem. Soc.* **1999**, *121*, 2599.
- [3] ^[3a] C. B. Aakeröy, K. R. Seddon, *Chem. Soc. Rev.* **1993**, *22*, 397. ^[3b] S. Subramanian, M. J. Zaworotko, *Coord. Chem. Rev.* **1994**, *137*, 357. ^[3c] S. Scheiner, *Hydrogen Bonding, A Theoretical Perspective*, Oxford University Press, Oxford, **1997**.
- [4] ^[4a] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1461. ^[4b] O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474. ^[4c] S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983.

- [5] ^[5a] G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, **1989**, ch. 4. ^[5b] C. A. Hunter, J. Singh, J. M. Thornton, *J. Mol. Biol.* **1991**, *218*, 837. ^[5c] A. S. Shetty, J. Zhang, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 1019.
- [6] ^[6a] C. B. Aakeröy, *Acta Crystallogr., Sect. B* **1997**, *53*, 569. ^[6b] P. Bhyrappa, S. R. Wilson, K. S. Suslick, *J. Am. Chem. Soc.* **1997**, *119*, 8492. ^[6c] K. Kobayashi, M. Koyanagi, K. Endo, H. Masuda, Y. Aoyama, *Chem. Eur. J.* **1998**, *4*, 417.
- [7] ^[7a] G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, New York, **1991**. ^[7b] A. D. Hamilton, *J. Chem. Educ.* **1990**, *67*, 821. ^[7c] M. M. Chowdhry, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Chem. Commun.* **1996**, 899. ^[7d] J. Bernstein, R. J. Davey, J. O. Henck, *Angew. Chem. Int. Ed.* **1999**, *38*, 3441–3461. ^[7e] J. Bernstein, *Polymorphism in Molecular Crystals* **2002**, Oxford University Press.
- [8] ^[8a] B. J. B. Folmer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1999**, *121*, 9001. ^[8b] B. Gong, Y. Yan, H. Zeng, E. Skrzypczak-Jankunn, Y. W. Kim, J. Zhu, H. Ickes, *J. Am. Chem. Soc.* **1999**, *121*, 5607. ^[8c] H. Zeng, R. S. Miller, R. A. Flowers, B. Gong, *J. Am. Chem. Soc.* **2000**, *122*, 2635.
- [9] ^[9a] X. Wang, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1994**, *116*, 12119. ^[9b] P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1997**, *119*, 2737.
- [10] M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, *J. Am. Chem. Soc.* **1996**, *118*, 3117.
- [11] ^[11a] C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *J. Am. Chem. Soc.* **1998**, *120*, 7383. ^[11b] I. L. Karle, D. Ranganathan, S. Kurur, *J. Am. Chem. Soc.* **1999**, *121*, 7156. ^[11c] C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *Angew. Chem. Int. Ed.* **1999**, *38*, 1815. ^[11d] N. C. Gianneschi, E. R. T. Tiekink, L. M. Rendina, *J. Am. Chem. Soc.* **2000**, *122*, 8474.
- [12] H. J. Choi, T. S. Lee, M. P. Suh, *Angew. Chem. Int. Ed.* **1999**, *38*, 1405.
- [13] ^[13a] H. J. Choi, M. P. Suh, *J. Am. Chem. Soc.* **1998**, *120*, 10622. ^[13b] H. J. Choi, M. P. Suh, *Inorg. Chem.* **1999**, *38*, 6309. ^[13c] K. S. Min, M. P. Suh, *Chem. Eur. J.* **2001**, *7*, 303. ^[13d] K. S. Min, M. P. Suh, *Eur. J. Inorg. Chem.* **2001**, 449. ^[13e] M. P. Suh, J. W. Ko, H. J. Choi, *J. Am. Chem. Soc.* **2002**, *124*, 10976. ^[13f] J. W. Ko, K. S. Min, M. P. Suh, *Inorg. Chem.* **2002**, *41*, 2151.

- [14] E. K. Barefield, F. Wagner, A. W. Herlinger, A. R. Dahl, *Inorg. Synth.* **1976**, 16, 220.
- [15] F. L. Urbach, in *Coordination Chemistry of Macrocyclic Compounds* (Ed.: G. A. Melson), Plenum Press, New York, **1979**, pp. 350–355.
- [16] L. J. Farrugia, ORTEP-3 for Windows, Version 1.03, University of Glasgow, Scotland, **1997**.
- [17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467.
- [18] G. M. Sheldrick, SHELXL-97, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.

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