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Syntheses, Crystal Structures, and Properties of Various One-Dimensional Coordination Polymers Based on Macrocyclic Metallic Tectons and Dicarboxylic Acid Ligand[1]

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Abstract—The reaction of different macrocyclic metallic tectons and dicarboxylic acid ligand yielded six new coordination polymers, namely, $\{[(NiL^1)(4,4'\text{-Bpdc})] \cdot DMF \cdot 2.5H_2O\}_n$ (**I**), $\{[(NiL^2)(4,4'\text{-Bpdc})] \cdot DMF \cdot 2.5H_2O\}_n$ (**II**), $[(NiL^3)_2(4,4'\text{-Bpdc})_{1.5}][(NiL^3)(4,4'\text{-Bpdc})] \cdot ClO_4 \cdot 28H_2O$ (**III**), $\{[(NiL^4)(4,4'\text{-Bpdc})] \cdot 4H_2O\}_n$ (**IV**), $\{[(NiL^5)(4,4'\text{-Tpdc})] \cdot 5H_2O\}_n$ (**V**), $\{[(NiL^3)(4,4'\text{-Tpdc})]\}_n$ (**VI**) (L^1 = 1,4,7,9,12,14-hexaaza-tricyclo[12.2.1.1$^{4.7}$]octadecane, L^2 = 1,3,10,12,15,18-hexaazatetracyclo[16.2.1.1$^{12.15}$.0$^{4.9}$]docosane, L^3 = 11-methyl-1,4,8,10,13,15-hexaaza-tricyclo[13.3.1.1$^{4.8}$]icosane, L^4 = 1,3,10,12,16,19-hexaazate-tracyclo[17.3.1.1.$^{12.16}$,0$^{4.9}$]tetracosane, L^5 = 1,4,8,10,13,15-hexaaza-tricyclo[13.3.1.1$^{4.8}$]icosane, 4,4'-Bpdc = 4,4'-biphenyldicarboxylic acid and 4,4'-Tpdc = 4,4'-terphenyldicarboxylic acid) (CIF files CCDC nos. 1055545–1055550 for **I**–**VI**, respectively). Except for the different conformations of the macrocyclic metallic tectons or dicarboxylic acid ligands, complexes **I**–**VI** crystallized under the same environment, however, they exhibit diverse packing mode of infinite 1D coordination polymers, showing macrocyle or dicarboxylic acid ligand regulated self-assemble. The solid states UV-Vis for complexes **I**–**VI** also have been investigated.

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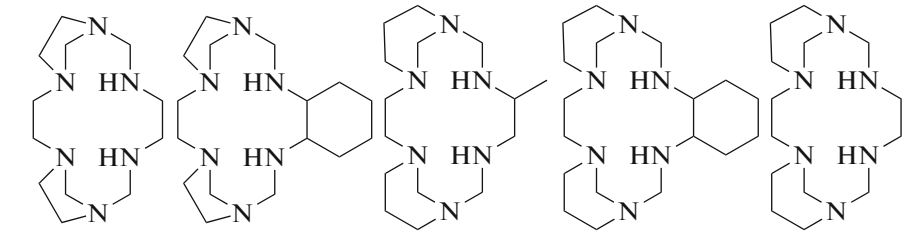
INTRODUCTION

Over the past decades, one-dimensional chains coordination polymers have gained numerous attentions due to their potential applications in molecular recognition [1, 2], magnetism [3–6], gas adsorption [7, 8], catalysis [9, 10] and so on. To obtain the one-dimensional coordination polymer, two basic elements are required, 2-connected linker and 2-connected node. Regarding the former aspect, those dicarboxylic acid ligands may serve as ideal linkers. To date, a few dicarboxylic acid ligands of such geometrical type have been utilized for the preparation of one-dimensional coordination polymers [11, 12]. Meanwhile, univalent coinage-metal ions Ag(I)/Cu(I) are often chosen as 2-connected nodes [13, 14]. Recent years, we and other groups focused on the macrocyclic metallic tecton, which also can be regarded as another 2-connected node choice in construction of such one-dimensional frameworks [15–17]. During the self-assembly, macrocyclic metallic tectons provide fixed numbers of vacant coordination sites at axial positions and enable the extending direction of the network to be controlled. Although the combination of dicarboxylic acid ligand and macrocyclic metallic tecton had been utilized by some groups, to date, work related to tune the packing mode of structure by change the conformation of macrocyclic metallic tecton have rarely been reported.

Herein, we report six new coordination complexes, namely, $\{[(NiL^1)(4,4'\text{-Bpdc})] \cdot DMF \cdot 2.5H_2O\}_n$ (**I**), $\{[(NiL^2)(4,4'\text{-Bpdc})] \cdot DMF \cdot 2.5H_2O\}_n$ (**II**), $[(NiL^3)_2(4,4'\text{-Bpdc})_{1.5}][(NiL^3)(4,4'\text{-Bpdc})](ClO_4) \cdot 28H_2O$ (**III**), $\{[(NiL^4)(4,4'\text{-Bpdc})] \cdot 4H_2O\}_n$ (**IV**), $\{[(NiL^5)(4,4'\text{-Tpdc})] \cdot 5H_2O\}_n$ (**V**), $\{[(NiL^3)(4,4'\text{-Tpdc})]\}_n$ (**VI**) (L^1 = 1,4,7,9,12,14-hexaaza-tricyclo[12.2.1.1$^{4.7}$]octadecane, L^2 = 1,3,10,12,15,18-hexaazatetracyclo[16.2.1.1$^{12.15}$.0$^{4.9}$]docosane, L^3 = 11-methyl-1,4,8,10,13,15-hexaaza-tricyclo[13.3.1.1$^{4.8}$]icosane, L^4 = 1,3,10,12,16,19-hexaazate-tracyclo[17.3.1.1.$^{12.16}$,0$^{4.9}$]tetracosane, L^5 = 1,4,8,10,13,15-hexaaza-tricyclo[13.3.1.1$^{4.8}$]icosane, 4,4'-Bpdc = 4,4'-biphenyldicarboxylic acid and 4,4'-Tpdc = 4,4'-terphenyldicarboxylic acid) based on various metallic macrocyclic precursors $[NiL^{1-5}](ClO_4)_2$ and dicarboxylic acid ligands. The structures of macrocyclic metallic tectons and dicarboxylic acid ligand are below:

[1] The article is published in the original.



L^1 L^2 L^3 L^4 L^5

4,4'-Bpdc 4,4'-Tpdc

Except for the different conformations of the macrocyclic metallic tectons or dicarboxylic acid ligands, complexes **I**–**VI** crystallized under the same environment, however, complexes exhibit diverse structures, showing macrocyles or dicarboxylic acid ligand regulated self-assemble.

EXPERIMENTAL

Materials and methods. All other chemicals are commercially available and were used without further purification. The macrocyclic complex precursor $[NiL^1](ClO_4)_2$ [18], $[NiL^2](ClO_4)_2$ [19], $[NiL^3](ClO_4)_2$ [20], $[NiL^4](ClO_4)_2$ [21] and $[NiL^5](ClO_4)_2$ [22] were prepared according to literatures. Elemental analyses were performed using a Vario ELIII CHNS/O elemental analyzer. The powder X-ray diffraction measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer. The IR spectra were measured from KBr pellets on a Nicolet Avatar 370 FT-IR spectrometer. Solid state UV-Vis diffuse reflectance spectra using samples diluted with $BaSO_4$ were recorded with a Shimadzu 2550 PC UV-Vis recording spectrophotometer.

Synthesis of I. A 2 mL DMF solution of $[NiL^1](ClO_4)_2$ (0.1 mmol) added to 5 mL water of Na_2(4,4'-Bpdc) (0.1 mmol), the solutions were mixed together with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within one month.

For $C_{29}H_{46}N_7O_{7.5}Ni$

anal. calcd., %:	C, 51.88;	H, 6.91;	N, 14.60.
Found, %:	C, 51.64;	H, 6.63;	N, 14.59.

IR (ν, cm^{-1}): 3341 s, 3200 s, 2890 w, 1577 s, 1541 s, 1493 m, 1391 s, 1272 m.

Synthesis of II. A 5 mL DMF solution of $[NiL^2](ClO_4)_2$ (0.1 mmol) added to 5 mL water of Na_2(4,4'-Bpdc) (0.1 mmol), the solution were mixed together with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within two days.

For $C_{33}H_{52}N_7O_{7.5}Ni$

anal. calcd., %:	C, 54.63;	H, 7.22;	N, 13.51.
Found, %:	C, 54.44;	H, 7.33;	N, 13.39.

IR (ν, cm^{-1}): 3406 s, 3198 s, 2858 w, 1588 s, 1540 s, 1464 m, 1391 s, 1271 m, 1041 s, 1007 s, 880 m, 674 m.

Synthesis of III. A 5 mL DMF solution of $[NiL^3](ClO_4)_2$ (0.1 mmol) added to 5 mL water of Na_2(4,4'-Bpdc) (0.1 mmol), the solutions were mixed together with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within two weeks.

For $C_{80}H_{173}N_{18}O_{43}ClNi_3$

anal. calcd., %:	C, 42.02;	H, 7.62;	N, 11.02.
Found, %:	C, 42.42;	H, 7.25;	N, 11.15.

IR (ν, cm^{-1}): 3346 s, 3188 s, 2853 w, 1589 s, 1545 s, 1461 m, 1382 s, 1001 s, 871 m, 778 m.

Synthesis of IV. A 1 mL DMF solution of $[NiL^4](ClO_4)_2$ (0.1 mmol) added to 9 mL water of Na_2(4,4'-Bpdc) (0.1 mmol), the solutions were mixed together with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within two weeks.

For $C_{32}H_{52}N_6O_8Ni$

anal. calcd., %:	C, 54.33;	H, 7.41;	N, 11.88.
Found, %:	C, 53.92;	H, 7.33;	N, 11.95.

IR (ν, cm^{-1}): 3345 s, 3199 s, 1587 s, 1540 s, 1462 m, 1380 s, 1270 m.

Synthesis of V. In a single tube, a DMF solution (10 mL) of $[NiL^5](ClO_4)_2$ (0.20 mmol) was layered with a aqueous solution (10 mL) of Na_2(4,4'-Tpdc)

Table 1. Crystallographic data and structure refinement parameters for **I**–**VI**

Parameter	Value					
	I	**II**	**III**	**IV**	**V**	**VI**
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$	*C*2/*c*	C2/*c*	$P2_1/n$
a, Å	22.8231(10)	27.7250(16)	12.6063(6)	18.536(4)	30.9906(17)	12.8057(8)
b, Å	10.2211(5)	15.0563(8)	19.9337(9)	20.523(4)	8.8443(5)	12.6198(6)
c, Å	29.4551(14)	18.3037(11)	21.6712(11)	20.202(4)	31.064(2)	19.9575(11)
α, deg	90	90	82.736(2)	90	90	90
β, deg	111.613(2)	114.456(2)	80.881(2)	107.39(3)	111.225(2)	90.390(2)
γ, deg	90	90	76.959(1)	90	90	90
Volume, Å^3	6388.1(5)	6955.1(7)	5214.9(4)	7334(3)	7936.8(8)	3225.2(3)
Z; ρ_{calcd}, mg/m^3	4, 1.386	4, 1.376	2, 1.134	8, 1.267	8, 1.100	4, 1.383
μ, mm^{-1}	0.665	0.617	0.622	0.583	0.528	0.651
F(000)	2816	3056	1884	2960	2784	1424
Reflections collected	18410	19293	58104	30967	22751	16894
Independent reflections	6156	6367	20086	7195	7196	5798
GOOF	1.03	1.05	1.11	1.05	1.12	1.08
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0525$, $wR_2 = 0.1296$	$R_1 = 0.0558$, $wR_2 = 0.1297$	$R_1 = 0.0673$, $wR_2 = 0.1888$	$R_1 = 0.1039$, $wR_2 = 0.2603$	$R_1 = 0.0659$, $wR_2 = 0.2189$	$R_1 = 0.0651$, $wR_2 = 0.1842$
Largest diff. peak and hole, *e* Å^{-3}	0.63 and −0.44	0.79 and −0.53	1.13 and −0.91	0.98 and −0.47	0.52 and −0.77	1.52 and −0.74

(0.20 mmol) at room temperature. After about two days, blue-purple crystals suitable for X-ray analysis were obtained.

For $C_{34}H_{52}N_6O_9Ni$

anal. calcd., %:	C, 54.63;	H, 7.01;	N, 11.24.
Found, %:	C, 54.81;	H, 7.35;	N, 11.41.

IR (ν, cm^{-1}): 3349 w, 2998 w, 1585 s, 1536 s, 1401 s, 1088 s, 994 m, 870 m, 772 m, 627 m.

Synthesis of VI. In a single tube, a DMF solution (10 mL) of $[NiL^3](ClO_4)_2$ (0.20 mmol) was layered with a aqueous solution (10 mL) of Na_2(4,4'-Tpdc) (0.20 mmol) at room temperature. After about three days, blue-purple crystals suitable for X-ray analysis were obtained.

For $C_{35}H_{44}N_6O_4Ni$

anal. calcd., %:	C, 62.61;	H, 6.60;	N, 12.52.
Found, %:	C, 62.71;	H, 6.63;	N, 12.50.

IR (ν, cm^{-1}): 1588 s, 1539 s, 1371 s, 1081 s, 984 m, 879 m, 768 m, 627 m.

X-ray crystallography. Single crystal X-ray diffraction data for complexes were collected on a Bruker Apex CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Absorption corrections were applied to the data using the SADABS program [23]. The structures were solved using SHELXL-97 and refined by full-matrix least-squares on F^2 [24, 25]. All non-hydrogen atoms of the networks were refined with anisotropic temperature parameters and hydrogen atoms were placed in calculated positions and refined with a riding model. The hydrogen atoms of discrete water molecule were not found from Fourier maps. Because of the disordered solvent molecules in complexes **III** and **V**, the SQUEEZE routine of PLATON was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities [26]. A final formula of complexes was derived from crystallographic data combined with elemental and SQUEEZE data. In complex **III**, one $[NiL^3]^{2+}$ moiety has crystallographically two-fold symmetry (0.5 occupancy of two CH_3 groups). Crystallographic data and structure determination summaries are listed in Table 1, and the selected bond lengths and angles for complexes **I**–**VI** are listed in Table 2.

Supplementary material for structures **I**–**VI** has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1055545 (**I**), 1055546 (**II**),

Table 2. Selected bond lengths (Å) and bond angles (deg)

I		**II**		**III**			
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Ni(1)–O(1)	2.181(3)	Ni(1)–O(1)	2.164(3)	Ni(1)–O(6)	2.076(3)	Ni(2)–O(1)	2.196(3)
Ni(1)–O(2)	2.161(3)	Ni(1)–O(2)	2.269(3)	Ni(1)–O(7)	2.202(3)	Ni(2)–O(3)	2.143(3)
Ni(1)–N(1)	2.044(3)	Ni(1)–N(1)	2.031(3)	Ni(1)–N(1)	2.062(4)	Ni(2)–N(8)	2.108(4)
Ni(1)–N(2)	2.043(3)	Ni(1)–N(2)	2.035(3)	Ni(1)–N(2)	2.073(4)	Ni(2)–N(9)	2.061(4)
Ni(1)–N(3)	2.105(3)	Ni(1)–N(3)	2.089(3)	Ni(1)–N(19)	2.118(4)	Ni(2)–N(10)	2.054(4)
Ni(1)–N(4)	2.092(3)	Ni(1)–N(4)	2.082(3)	Ni(1)–N(21)	2.137(4)	Ni(2)–N(11)	2.129(4)
Angle	deg	Angle	deg	Angle	deg	Angle	deg
O(1)Ni(1)O(2)	178.08(9)	O(1)Ni(1)O(2)	173.16(9)	O(6)Ni(1)O(7)	176.84(12)	O(1)Ni(2)O(3)	176.90(13)
O(1)Ni(1)N(1)	88.79(11)	O(1)Ni(1)N(1)	89.58(12)	O(6)Ni(1)N(1)	94.58(12)	O(1)Ni(2)N(8)	88.90(12)
O(1)Ni(1)N(2)	89.02(11)	O(1)Ni(1)N(2)	88.55(12)	O(6)Ni(1)N(2)	92.11(12)	O(1)Ni(2)N(9)	92.56(13)
O(1)Ni(1)N(3)	94.20(11)	O(1)Ni(1)N(3)	96.69(11)	O(6)Ni(1)N(19)	89.31(12)	O(1)Ni(2)N(10)	92.03(13)
O(1)Ni(1)N(4)	87.15(11)	O(1)Ni(1)N(4)	87.25(11)	O(6)Ni(1)N(21)	87.49(13)	O(1)Ni(2)N(11)	87.60(12)
O(2)Ni(1)N(1)	91.59(11)	O(2)Ni(1)N(1)	86.33(12)	O(7)Ni(1)N(1)	87.35(12)	O(3)Ni(2)N(8)	89.17(13)
O(2)Ni(1)N(2)	89.12(11)	O(2)Ni(1)N(2)	85.78(12)	O(7)Ni(1)N(2)	85.51(12)	O(3)Ni(2)N(9)	89.99(14)
O(2)Ni(1)N(3)	87.67(11)	O(2)Ni(1)N(3)	89.02(11)	O(7)Ni(1)N(19)	93.08(12)	O(3)Ni(2)N(10)	89.90(14)
O(2)Ni(1)N(4)	92.54(11)	O(2)Ni(1)N(4)	96.96(11)	O(7)Ni(1)N(21)	90.55(13)	O(3)Ni(2)N(11)	89.88(14)
N(1)Ni(1)N(2)	86.65(12)	N(1)Ni(1)N(2)	87.25(12)	N(1)Ni(1)N(2)	86.41(15)	N(8)Ni(2)N(9)	93.92(15)
N(1)Ni(1)N(3)	92.59(12)	N(1)Ni(1)N(3)	93.23(11)	N(1)Ni(1)N(19)	93.36(15)	N(8)Ni(2)N(10)	179.07(14)
N(1)Ni(1)N(4)	175.53(13)	N(1)Ni(1)N(4)	176.55(14)	N(1)Ni(1)N(21)	177.78(13)	N(8)Ni(2)N(11)	86.80(15)
N(2)Ni(1)N(4)	176.68(13)	N(2)Ni(1)N(4)	174.74(14)	N(2)Ni(1)N(21)	178.58(13)	N(9)Ni(2)N(10)	86.05(16)
N(2)Ni(1)N(4)	95.12(12)	N(2)Ni(1)N(4)	94.03(12)	N(2)Ni(1)N(21)	92.69(15)	N(9)Ni(2)N(11)	179.26(16)
N(3)Ni(1)N(4)	85.87(12)	N(3)Ni(1)N(4)	85.79(11)	N(19)Ni(1)N(21)	87.50(14)	N(10)Ni(2)N(11)	93.22(15)
III		**IV**		**V**		**VI**	
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Ni(3)–O(8)	2.103(4)	Ni(1)–O(1)	2.138(4)	Ni(1)–O(1)	2.164(4)	Ni(1)–O(1)	2.165(3)
Ni(3)–O(10)	2.095(3)	Ni(1)–O(4)	2.158(4)	Ni(1)–O(3)	2.141(3)	Ni(1)–O(3)	2.178(3)
Ni(3)–N(16)	2.065(5)	Ni(1)–N(1)	2.054(6)	Ni(1)–N(1)	2.101(4)	Ni(1)–N(2)	2.052(4)
Ni(3)–N(20)	2.137(4)	Ni(1)–N(2)	2.046(4)	Ni(1)–N(2)	2.129(3)	Ni(1)–N(3)	2.121(4)
Ni(3)–N(13)	2.141(4)	Ni(1)–N(3)	2.121(6)	Ni(1)–N(3)	2.045(6)	Ni(1)–N(5)	2.063(4)
Ni(3)–N(15)	2.039(4)	Ni(1)–N(4)	2.128(6)	Ni(1)–N(4)	2.065(4)	Ni(1)–N(6)	2.120(4)
Angle	deg	Angle	deg	Angle	deg	Angle	deg
O(10)Ni(3)N(15)	93.20(15)	O(1)Ni(1)O(4)	177.27(17)	O(1)Ni(1)O(3)	175.47(11)	O(1)Ni(1)O(3)	178.36(11)
O(10)Ni(3)N(16)	92.51(16)	O(1)Ni(1)N(1)	91.7(2)	O(1)Ni(1)N(1)	93.36(15)	O(1)Ni(1)N(2)	90.90(14)
O(10)Ni(3)N(20)	87.47(15)	O(1)Ni(1)N(2)	90.9(2)	O(1)Ni(1)N(2)	96.93(12)	O(1)Ni(1)N(3)	89.74(12)
N(13)Ni(3)N(15)	94.28(18)	O(1)Ni(1)N(3)	89.1(2)	O(1)Ni(1)N(3)	85.83(19)	O(1)Ni(1)N(5)	89.59(12)
N(13)Ni(3)N(16)	179.47(17)	O(1)Ni(1)N(4)	88.5(2)	O(1)Ni(1)N(4)	83.76(16)	O(1)Ni(1)N(6)	88.72(14)
N(13)Ni(3)N(20)	87.41(17)	O(4)Ni(1)N(1)	90.8(2)	O(3)Ni(1)N(1)	87.57(13)	O(3)Ni(1)N(2)	90.11(14)
N(15)Ni(3)N(16)	86.20(18)	O(4)Ni(1)N(2)	90.2(2)	O(3)Ni(1)N(2)	87.54(12)	O(3)Ni(1)N(3)	88.93(12)
N(15)Ni(3)N(20)	178.21(18)	O(4)Ni(1)N(3)	89.8(2)	O(3)Ni(1)N(3)	93.19(18)	O(3)Ni(1)N(5)	91.77(12)
N(16)Ni(3)N(20)	92.12(18)	O(4)Ni(1)N(4)	88.93(19)	O(3)Ni(1)N(4)	91.78(16)	O(3)Ni(1)N(6)	90.28(14)
O(10)Ni(3)N(13)	87.25(15)	N(1)Ni(1)N(2)	85.9(2)	N(1)Ni(1)N(2)	87.55(14)	N(2)Ni(1)N(3)	92.54(15)
O(8)Ni(3)N(15)	91.48(16)	N(1)Ni(1)N(3)	94.0(3)	N(1)Ni(1)N(3)	178.95(19)	N(2)Ni(1)N(5)	85.69(18)
O(8)Ni(3)O(10)	173.94(14)	N(1)Ni(1)N(4)	179.6(3)	N(1)Ni(1)N(4)	92.41(19)	N(2)Ni(1)N(6)	179.41(15)
O(8)Ni(3)N(13)	88.56(15)	N(2)Ni(1)N(4)	179.9(3)	N(2)Ni(1)N(4)	93.22(16)	N(3)Ni(1)N(5)	178.10(18)
O(8)Ni(3)N(16)	91.65(16)	N(2)Ni(1)N(4)	93.8(2)	N(2)Ni(1)N(4)	179.32(18)	N(3)Ni(1)N(6)	87.91(15)
O(8)Ni(3)N(20)	87.96(15)	N(3)Ni(1)N(4)	86.4(3)	N(3)Ni(1)N(4)	86.8(2)	N(5)Ni(1)N(6)	93.85(17)

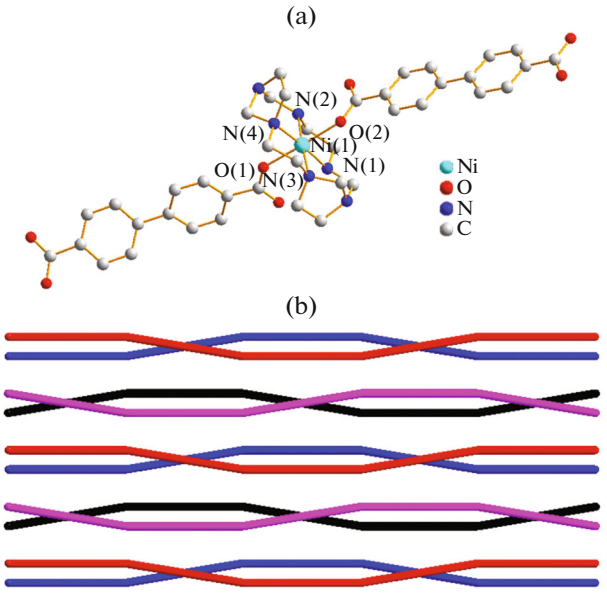


Fig. 1. The molecular structure diagram of complex **I** with the selected atom-labeling scheme (a); ABCDABCD sequence in complex **I** (b).

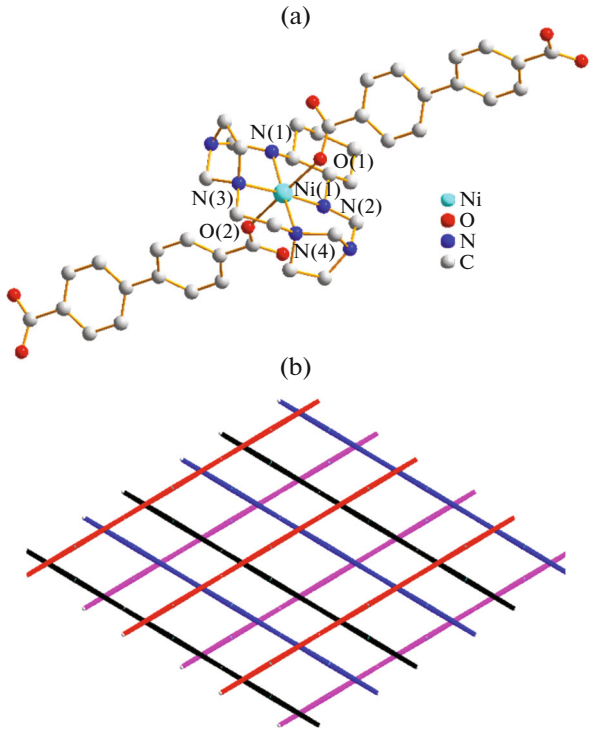


Fig. 2. The molecular structure diagram of complex **II** with the selected atom-labeling scheme (a); cross-like arrangement of ABCDABCD sequence in complex **II** (b).

1055547 (**III**), 1055548 (**IV**), 1055549 (**V**) and 1055550 (**VI**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown in Fig. 1a, single-crystal X-ray diffraction analysis reveals that complex **I** consists of one 4,4'-Bpdc^{2-} anion, one $[NiL^1]^{2+}$ cation, one DMF and two and a half of water molecules. The coordination geometry around nickel(II) atom is described best by a slightly $[NiN_4O_2]$ distorted octahedron with four Ni–N bonds from the macrocycle and two Ni–O bonds from 4,4'-Bpdc^{2-} ligands. The average Ni(1)–N and Ni(1)–O bond distances are 2.071 and 2.171 Å, respectively, which range in the normal distances compared to similar complexes. Each 4,4'-Bpdc^{2-} binds two $[NiL^1]^{2+}$ fragments in a bis-monodentate mode, which results in a tortuous 1D coordination polymer chain. Those 1D chains are further held together through inter-chains hydrogen bonds, giving rise to a 3D supramolecular structure. The packing of 1D chain polymers occurs with a parallel orientation of all chains with ABCDABCD sequence (Fig. 1b).

Similar to complex **I**, the X-ray crystal structure of **II** shows a neutral 1D chain with a basic repeated unit (NiL^2)(4,4'-Bpdc) (Fig. 2a). The Ni^{2+} ion is located on the inversion center with $[NiN_4O_2]$ octahedral coordination geometry, where four secondary nitrogen atoms from the macrocycle and two oxygen atoms from the 4,4'-Bpdc^{2-} ligands. The average Ni(1)–N and Ni(1)–O bond distances are 2.059 and 2.217 Å, respectively. Each 4,4'-Bpdc^{2-} binds two $[NiL^2]^{2+}$ fragments in a bis-monodentate mode, which results in a straight 1D coordination polymer chain. In complex **II**, different series of 1D chain extend in different directions and pack alternately in nonparallel fashion with cross-like arrangement, forming a rare 3D plywood-like array with ABCDABCD sequence (Fig. 2b). To date, the packing of 1D chain polymers usually occurs with a parallel orientation of all chains, such as complex **I**, they can rarely extend along two different directions with cross-like arrangement, let alone with the quadruple 1D chains in two different directions.

The molecular structure of complex **III** with atom labeling is shown in Fig. 3a. Complex **III** consists of tetranuclear $[(NiL^3)_4(4,4'\text{-Bpdc})_3]^{2+}$ cation, a neutral 1D chain with (NiL^3)(4,4'-Bpdc) repeat unit, perchlorate ions and several disordered water molecules. Similar to complexes **I** and **II**, all nickel(II) atoms sit on an coordination center, which displays distorted $[NiN_4O_2]$ octahedral geometry with four secondary nitrogens from the macrocyclic liagnd L^3 and two oxygens from carboxylates or coordinated water molecules. As shown in Fig. 3b, tetranuclear $[(NiL^3)_4(4,4'\text{-Bpdc})_3]^{2+}$ fragments are linked by hydrogen bonds from the coordinated water molecule (O(7)) and nitrogen on the macrocyclic ligand (N(22)), giving rise to a infinite 1D chain (Fig. 3b). In complex **III**, all

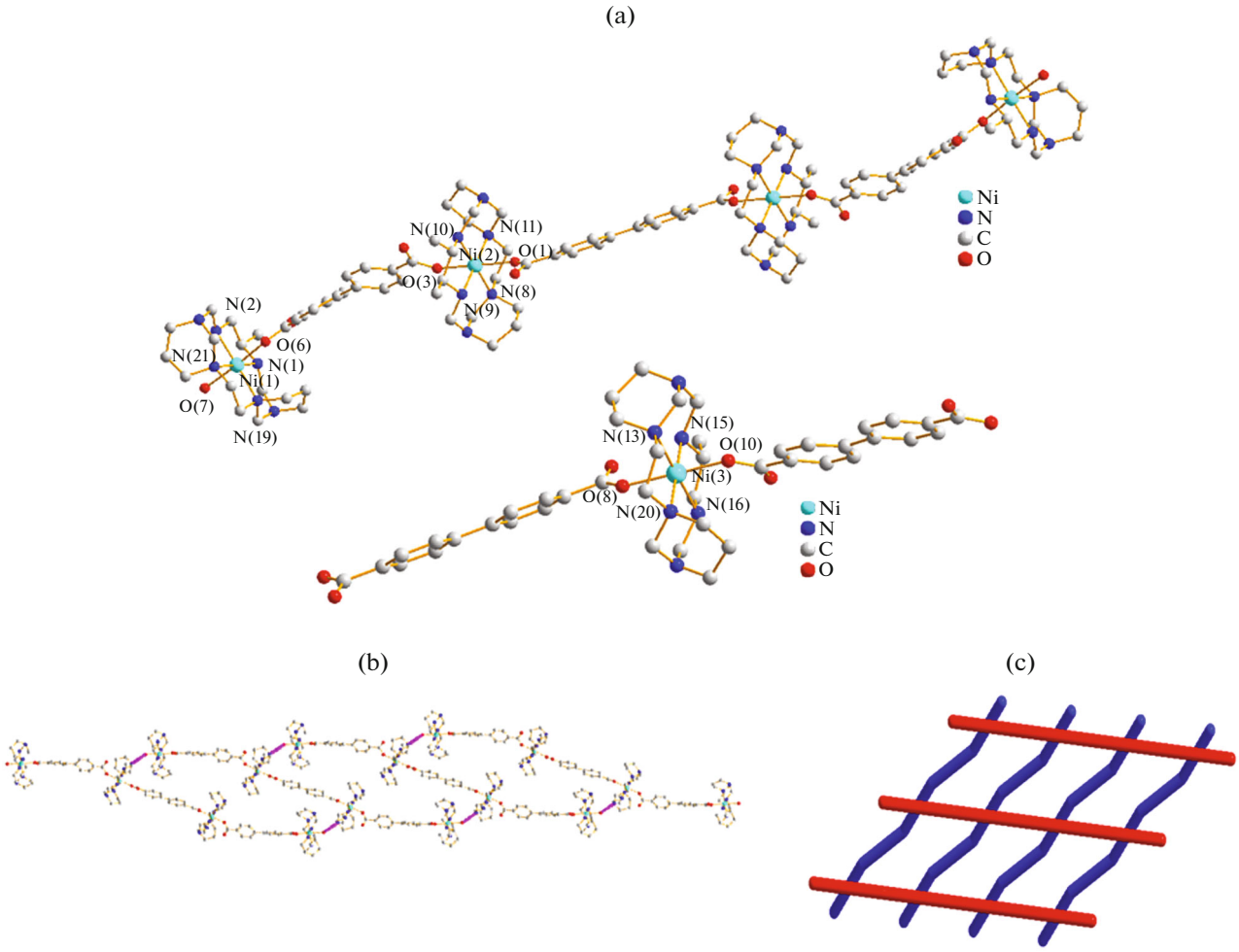


Fig. 3. The molecular structure diagram of two fragments in complex **III** with the selected atom-labeling scheme (a), hydrogen bonds between $[(NiL^3)_4(4,4'\text{-Bpdc})_3]^{2+}$ cation (b), ABAB sequence in complex **III** (c).

1D chains pack alternately in nonparallel fashion with rare cross-like arrangement, forming a 3D pseudo plywood-like array with ABAB sequence (Fig. 3c).

The X-ray crystal structure of complex **IV** shows that the Ni^{2+} ion is coordinated by four nitrogen atoms of the L^4 and that the axial positions are bonded by two oxygen atoms from the 4,4'-$Bpdc^{2-}$ ligands to furnish a distorted $[NiN_4O_2]$ octahedral geometry (Fig. 4a). The average Ni(1)–N and Ni(1)–O bond distances are 2.087 and 2.148 Å, respectively. Each 4,4'-$Bpdc^{2-}$ anion binds two Ni^{2+} ions in a bis-monodentate mode, and each $[NiL^4]^{2+}$ ion is coordinated to two carboxylate oxygen atoms of 4,4'-$Bpdc^{2-}$ which results in a 1D coordination polymer chain. Furthermore, those 1D coordination chains in complex **IV** ranks in sole direction with ABCABC sequence (Fig. 4b). Interestingly, a water cube is observed in complex **IV**. The hydrogen bonding association of water molecules leads to the formation of a cube of water clusters (Fig. 4c). The O···O distances within the range from 2.833 to 2.925 Å, which are well comparable with the values obtained from the *ab initio* calculations [27].

Complexes **I**–**IV** is constructed based on 4,4'-Bpdc ligand. To extend this series, 4,4'-Tpdc with three benzene rings was utilized, hence, complexes **V**, **VI** were isolated. Similar to complexes **I**, **II** and **IV**, the X-ray crystal structure of **V** shows a neutral 1D chain with a basic repeated unit (NiL^5)(4,4'-Tpdc) (Fig. 5a). The Ni^{2+} ion is also located on the inversion center with $[NiN_4O_2]$ octahedral coordination geometry, where four secondary nitrogen atoms from the L^5 and two oxygen atoms from two different 4,4'-$Tpdc^{2-}$ ligands. The average Ni(1)–N and Ni(1)–O bond distances are 2.085 and 2.153 Å, respectively. Each 4,4'-$Bpdc^{2-}$ binds two $[NiL^5]^{2+}$ fragments in a bis-monodentate mode, which results in a straight 1D coordination polymer chain. In complex **V**, 1D chians pack alternately in different direction, forming a unique array with ABAB sequence (Fig. 5b). By such array, 1D porous channel is observed along *z* axis (Fig. 5c).

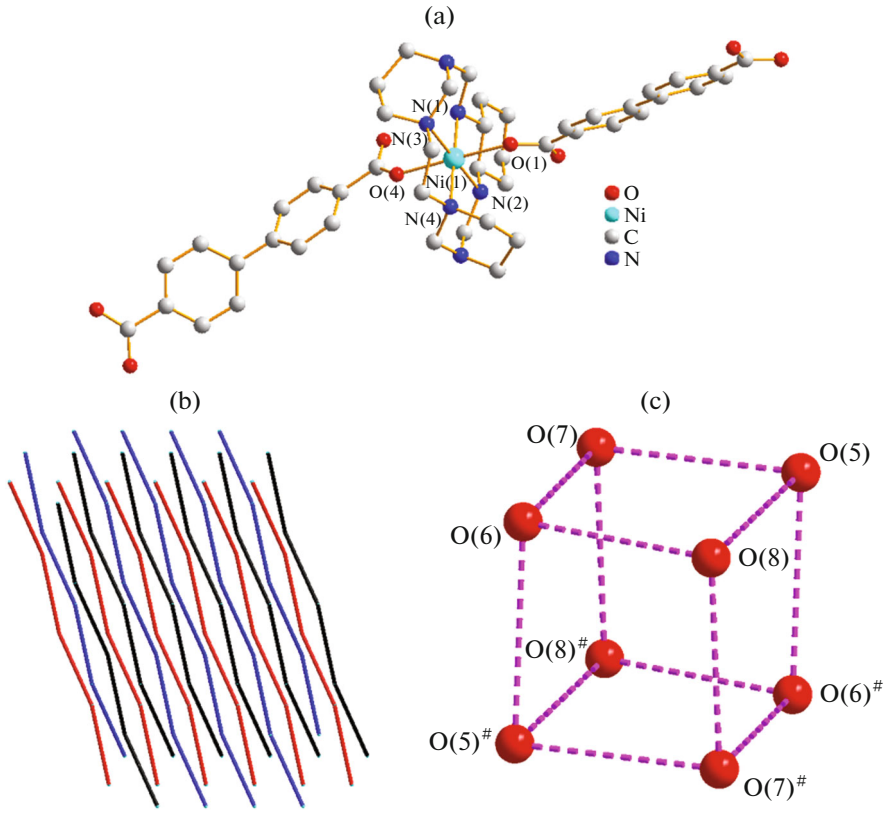


Fig. 4. The molecular structure diagram of complex **IV** with the selected atom-labeling scheme (a), ABCABC sequence in complex **IV** (b), water cube in complex **IV** (c).

As shown in Fig. 6a, single-crystal X-ray diffraction analysis reveals that complex **VI** consists of one 4,4'-Tpdc^{2-} anion, one $[NiL^3]^{2+}$ cation without any guests. The Ni^{2+} ion is also located on the inversion center with $[NiN_4O_2]$ octahedral coordination geometry, where four secondary nitrogen atoms from the L^3 and two oxygen atoms from two different 4,4'-Tpdc^{2-} ligands. The average Ni(1)–N and Ni(1)–O bond distances are 2.089 and 2.172 Å, respectively. Each 4,4'-Bpdc^{2-} binds two $[NiL^3]^{2+}$ fragments in a bis-monodentate mode resulting in a straight 1D coordination polymer chain. In complex **VI**, 1D chians pack alternately in one direction with ABCDABCD sequence (Fig. 6b).

It had been proved that the crystallization of targeted complexes is obviously influenced by various conditions, such as pH, solvent and temperature and so on. In the report, except the macrocyclic metallic tectons or dicarboxylic acid ligands, complexes **I**–**VI** were synthesized under the same external experimental environment (solvent, temperature and ratios of raw materials), however, complexes exhibit various packing modes of 1D chain. The comparison shows the macrocyles and/or dicarboxylic acid ligand regulated self-assemble.

The comparisons of simulated and experimental XRD patterns of those complexes are shown that their peak positions are in good consistency with each other, indicating the phase purity of the samples. The solid state UV-Vis diffuse reflectance spectra of complexes **I**–**VI** exhibit strong broad peaks at 527, 544, 542, 525 and 500 nm in visible region, respectively, are depicted in Fig. 7. Compared to their precursor macrocyclic metallic tectons $[NiL^{1-5}](ClO_4)_2$, the red-shift of wavelengths of the d–d^* transition verify the six-coordinated octahedral geometry of complexes.

In summary, six different Ni(II) coordination complexes based on various macrocyclic metallic tectons and dicarboxylic acid ligand were obtained and characterized. The result shows a macrocyles or dicarboxylic acid ligand induced different supramolecular self-assembly. Finally, they exhibit diverse packing mode based on infinite 1D coordination polymers.

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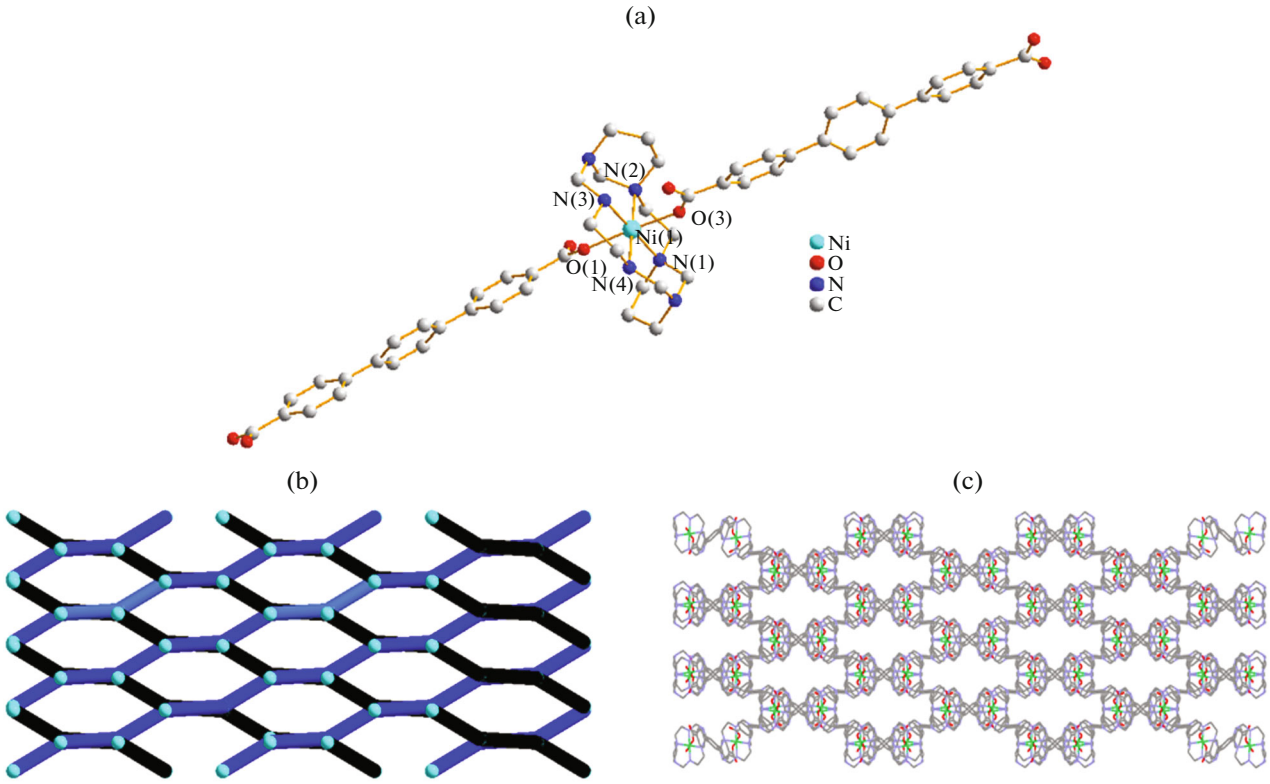

Fig. 5. The molecular structure diagram of complex **V** with the selected atom-labeling scheme (a), ABAB sequence in complex **V** (b), 1D porous channel in complex **V** (c).

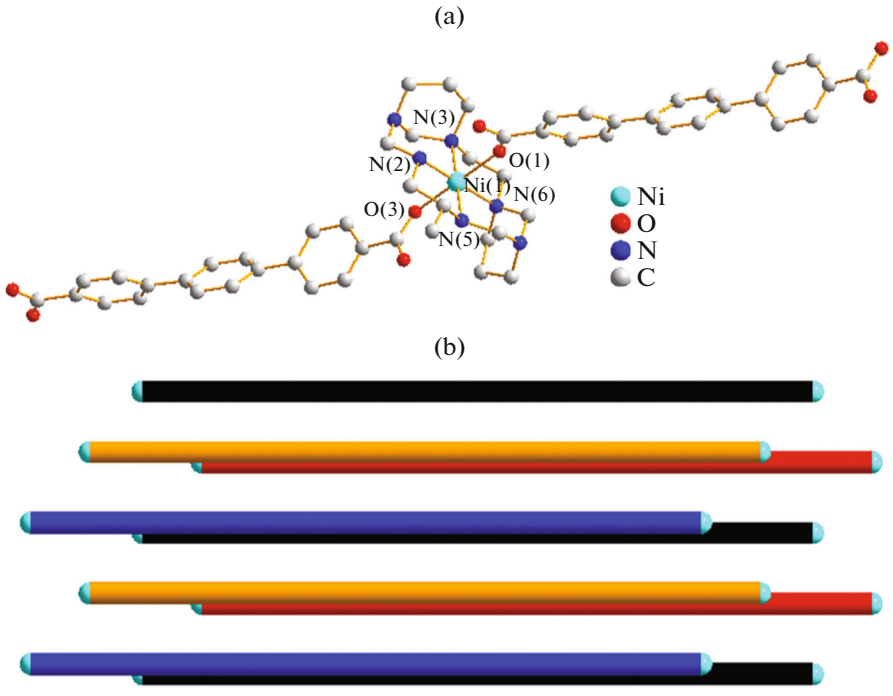

Fig. 6. The molecular structure diagram of complex **VI** with the selected atom-labeling scheme (a), ABCDABCD sequence in complex **VI** (b).

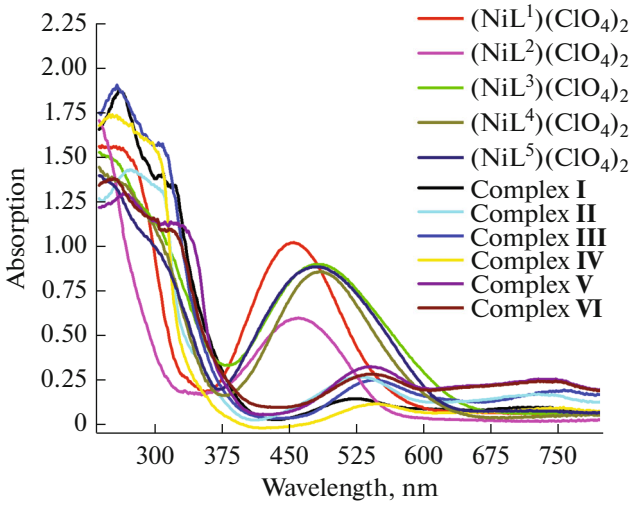

Fig. 7. Solid states UV-Vis of macrocyclic precursors and complexes **I**–**VI**.

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