Supporting Information

Position of Substituent Dependent Dimensionality in Ln-Cu Heterometallic Coordination Polymers

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Measure Method and Apparatus.

All reagents except *L*-alanine-N-monoacetic acid were of commercial origin and were used as received. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The infrared spectra were recorded on a Nicolet AVATAR FT-IR360 Spectrophotometer with pressed KBr pellets. TGA curves were prepared on a SDT Q600 Thermal Analyzer. Magnetic measurements were performed by a Quantum Design MPMS superconducting quantum interference device (SQUID).

Single crystals having suitable dimensions for compounds **1-2, 4** and **6** were used for data collection using a CrysAlis CCD diffractometer at 173 K equipped with Enhance (Mo) X-ray Source (λ = 0.71073 Å). Integration and cell refinement were carried out using CrysAlis RED. The absorption corrections were performed by multiscan method using SCALE3 ABSPACK scaling algorithm. Compound **3** and **5** were used for data collection using a Rigaku RAXIS-CS Imaging Plate at 298 K equipped with Mo X-ray Source (λ = 0.71073 Å). Integration and cell refinement were carried out using R-AXIS-SPIDER. The absorption corrections were performed by multiscan method using Tompa analytical method. Corrections were made for Lorentz and polarization effects. The molecular structures were solved by direct methods (SHELXL-86/SHELXL-97) and refinement by full-matrix least-squares on F^2 (SHELXS-97). Due to the disorder methyl of $ANMA^{2-}$ ligand in compounds 1-**3**, both –$C(5)H_3$ and –$C(6)H_3$ methyl are assigned half-occupancy, which results in error count of H atoms for $ANMA^{2-}$ ligand."

Synthesis Methods

Synthesis of H_2ANMA: *L*-alanine-N-monoacetic acid hydrochloride (H_2ANMA.HCl.0.25H_2O, Mw=188) was prepared based on Okamoto's method [1]. Anal. Calcd (found): C: 32.08 (31.95); H: 5.34(5.55); N: 7.44(7.53). H-NMR(DMSO)**:** δ 1.62(D,3H), δ 4.00(S,1H), δ 4.15(Q,2H).

Synthesis of {[La_2Cu_3(ANMA)$_6$]$(H_2O)_3$}(1): 0.246 g $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 mmol) and 0.376 g H_2ANMA.HCl.0.25H_2O (2.0 mmol) were dissolved in 10 mL of deionized water while stirring for 10 min. Then, to the solution were added 0.290 g $La(NO_3)_3 \cdot 6H_2O$ (0.67mmol). The pH value of the mixture was slowly adjusted to about 5.0 to 5.5 with 1.0 mol L^{-1} sodium hydroxide solution. The mixture was subsequently transferred to 18 mL Teflon-lined Parr, heated to 130 ^oC for 30 min, then cooled to room temperature at a rate of 2 $^oC \cdot h^{-1}$. Block blue crystals of **1** were obtained in about 48 % yield (based on $La(NO_3)_3$). Anal. Calcd (found) for **1**, $C_{30}H_{48}O_{27}N_6La_2Cu_3$ (%):C, 25.84 (25.77); H, 3.45 (2.99); N, 6.03 (6.05). IR (KBr, cm^{-1}): 539(w), 605(w), 733(w), 780(m), 854(w), 909(w), 998(w), 1029(m), 1064(w), 1119(w), 1158(m), 1240(w), 1278(w), 1317(w), 1337(w), 1384(m), 1403(m), 1450(w), 1566(s), 1572(s), 2365(w), 2802(w), 2933(w), 3190(w), 3447(s).

Synthesis of {[Pr_2Cu_3(ANMA)$_6$]$(H_2O)_3$}(2): This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.292g (0.67 mmol) $Pr(NO_3)_3 \cdot 6H_2O$ in place of $La(NO_3)_3 \cdot 6H_2O$. The product was obtained as block-shaped blue crystals in about 46 % yield (based on $Pr(NO_3)_3$). Anal. Calcd (found) for **2**, $C_{30}H_{48}O_{27}N_6Pr_2Cu_3$ (%): C, 25.76 (25.81); H, 3.43 (2.99); N, 6.01 (6.16). IR (KBr, cm^{-1}): 541(w), 605(w), 737(w), 784(w), 850(w), 905(w), 998(w), 1029(w), 1076(w), 1127(w), 1150(m), 1247(w), 1278(w), 1337(w), 1384(m), 1407(m), 1450(w), 1570(s), 1625(s), 2929(w), 3197(w), 3443(s).

Synthesis of {[Nd_2Cu_3(ANMA)$_6$]$(H_2O)_3$}(3): This compound was prepared using the same procedure as described above for the synthesis of its La(III) cognate, but using 0.294g (0.67 mmol) $Nd(NO_3)_3 \cdot 6H_2O$ in place of $La(NO_3)_3 \cdot 6H_2O$. The product was obtained as block-shaped blue crystals in about 37 % yield (based on $Nd(NO_3)_3$). Anal. Calcd (found) for **3**, $C_{30}H_{48}O_{27}N_6Nd_2Cu_3$ (%):C, 25.64 (25.85); H, 3.41 (3.25); N, 5.98 (6.09). IR (KBr, cm^{-1}): 539(w), 605(w), 737(w), 784(w), 850(w), 909(w), 994(w), 1037(w), 1068(w), 1123(w), 1154(w), 1243(w), 1278(w), 1329(w), 1333(w), 1403(w), 1442(w), 1570(s), 1625(s), 2933(w), 3186(s).

Synthesis of {[$La_2Cu(MIDA)_4(H_2O)_6$]$(H_2O)_4$}(4): This compound was prepared using the same procedure as described above for the synthesis of (**1**), except using 0.294g (2.0 mmol) H_2MIDA in place of H_2ANMA. The product was obtained as block-shaped blue crystals in about 45 % yield (based on $La(NO_3)_3$). Anal. Calcd (found) for **4**, $C_{20}H_{48}O_{26}N_4$ La_2Cu (%):C, 21.77 (21.65); H, 4.36 (4.43); N, 5.08 (4.98). IR (KBr, cm^{-1}): 551(w), 664(w), 738(m), 894(m), 940(w), 1024(w), 1139(w), 1201(m), 1244(m), 1326(s), 1415(m), 1431(m), 1458(m), 1587(s), 1660(w), 2812(w), 2921(w).

Synthesis of {[$Pr_2Cu(MIDA)_4(H_2O)_6$]$(H_2O)_4$} (5): This compound was prepared using the same procedure as described above for the synthesis of of its La(III) cognate (**4**), except using 0.292g (0.67 mmol) $Pr(NO_3)_3\cdot6H_2O$ in place of $La(NO_3)_3\cdot6H_2O$. The product was obtained as block-shaped blue crystals in about 40 % yield (based on $Pr(NO_3)_3$). Anal. Calcd (found) for **5**, $C_{20}H_{48}O_{26}N_4$ Pr_2Cu (%): C, 21.70 (21.33); H, 4.34 (4.87); N, 5.06 (4.96). IR (KBr, cm^{-1}): 559(w), 676(w), 738(w), 894(w), 940(w), 1049(w), 1143(w), 1197(w), 1244(m),1279(w), 1326(s), 1415(m), 1431(w), 1458(m), 1571(s), 1653(w), 2809(w), 2929(w), 2964(w).

Synthesis of {[$Nd_2Cu(MIDA)_4(H_2O)_6$]$(H_2O)_4$} (6): This compound was prepared using the same procedure as described above for the synthesis of of its La(III) cognate (**4**), except using 0.294g (0.67 mmol) $Nd(NO_3)_3\cdot6H_2O$ in place of $La(NO_3)_3\cdot6H_2O$. The product was obtained as block-shaped blue crystals in about 31 % yield (based on $Nd(NO_3)_3$). Anal. Calcd (found) for **6**, $C_{20}H_{48}O_{26}N_4Nd_2Cu$ (%): C, 21.57 (21.55); H, 4.31 (4.25); N, 5.03 (4.99). IR (KBr, cm^{-1}): 557(w), 662(w), 737(w), 893(w), 938(w), 989(w), 1043(w), 1098(w), 1113(w), 1137(w), 1199(w), 1244(w), 1279(w),1328(m), 1413(w), 1431(w), 1461(w), 1576(s), 1661(w), 2810(w), 2926(w), 2968(w).

3D supermolecule structure for complex 4

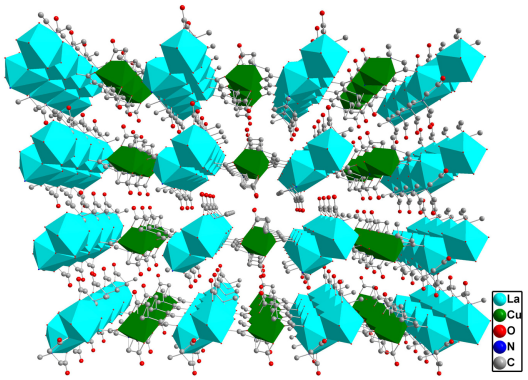

Figure S1 Polyhedron view of three-dimensional supermolecule structure for **4**

Magnetic properties for Compounds 2-3 and 5-6

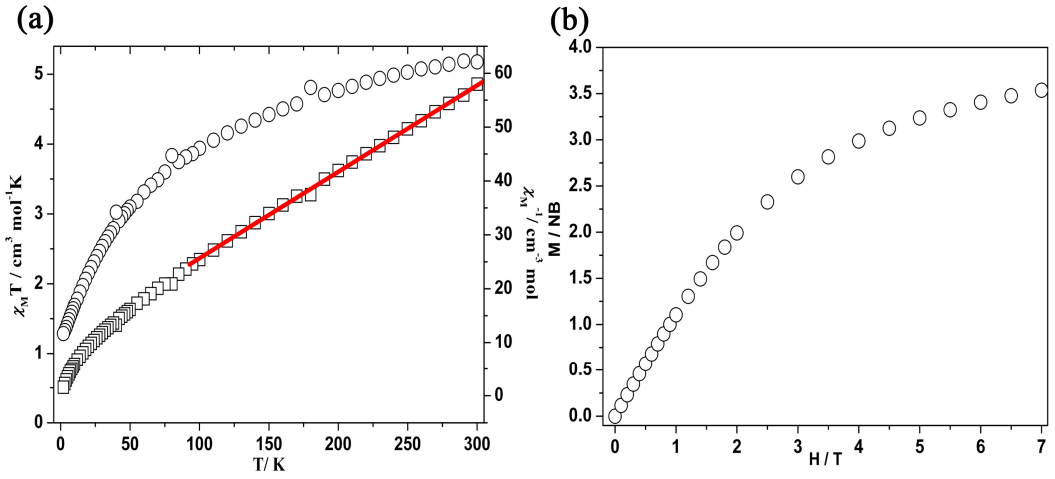

Figure S2 (a) Plots of $\chi_M T$ *vs* T (donated ○), red solid line fittd for χ_M^{-1} *vs* T (donated □) of **2**;(b) Plot of M *vs* H for compound **2**.

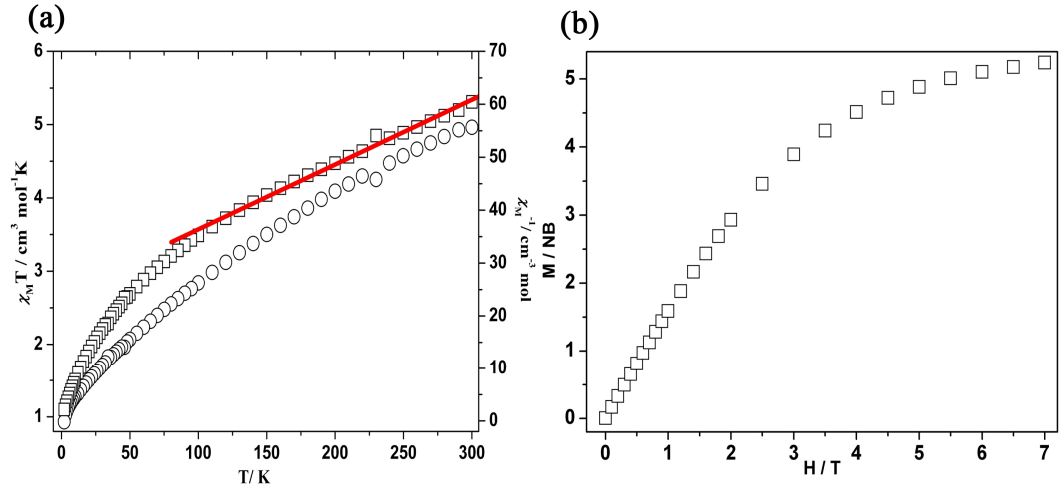

Figure S3 (a) Plots of $\chi_M T$ *vs* T (donated ○), red solid line fittd for χ_M^{-1} *vs* T (donated □) of **3**;(b) Plot of M *vs* H for compound **3**.

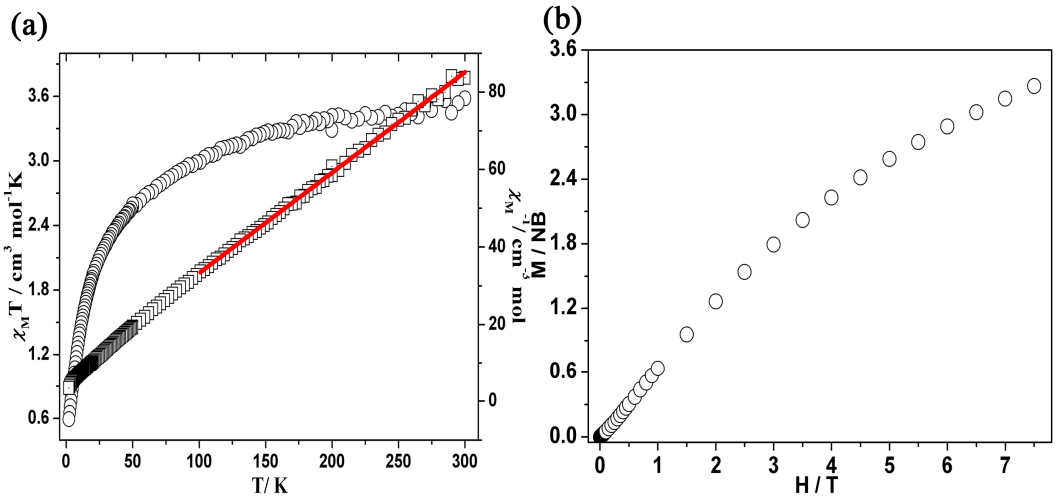

Figure S4 (a) Plots of $\chi_M T$ *vs* T (donated ○), red solid line fittd for χ_M^{-1} *vs* T (donated □) of **5**;(b) Plot of M *vs* H for compound **5**.

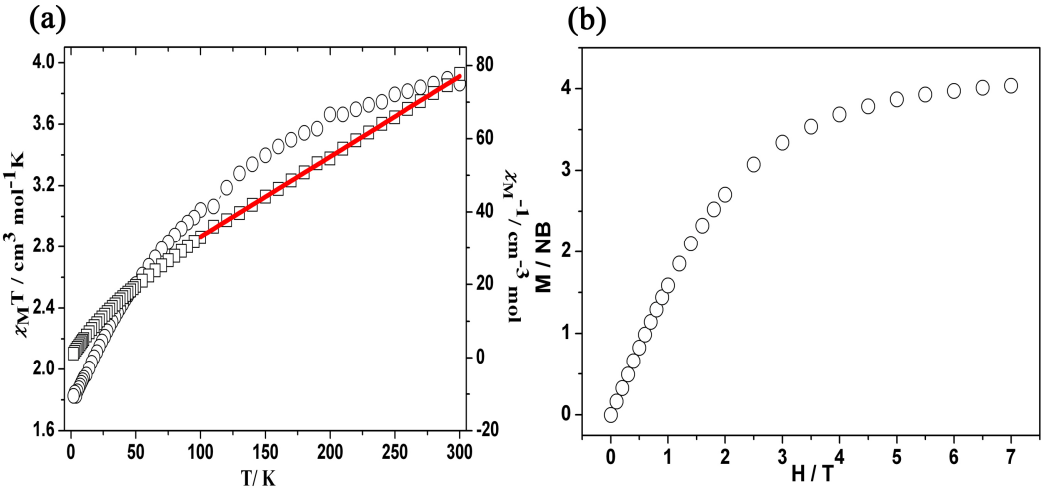

Figure S5 (a) Plots of $\chi_M T$ *vs* T (donated ○), red solid line fittd for χ_M^{-1} *vs* T (donated □) of **6**;(b) Plot of M *vs* H for compound **6**.

1. K. I. Okamoto, J. Hidaka, Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1601.