#### SUPPLEMENTAL INFORMATION

### X-Ray Crystallographic Data Collection and Refinement

All X-Ray intensity data were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). Raw area detector data frame reduction and corrections for absorption effects were performed with the SAINT+ and SADABS programs. Final unit cell parameters were determined by least-squares refinement of large sets of reflections from each data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F<sup>2</sup> were performed with SHELXTL. X-ray crystallographic data are given in Table S1.

 $[Cu_2(L_{ala})_4(THF)_2]$  (1) crystallizes as blue prisms in the space group *P*6<sub>3</sub> as determined by the pattern of systematic absences in the intensity data and by the fixed chirality of the ligands used. The asymmetric unit consists of one  $[Cu_2(L_{ala})_4(THF)_2]$  complex, three uncoordinated THF and one hexane molecule of crystallization. The three THF molecules are disordered. The coordinated THF O6 is disordered over two 'envelope' conformations with populations A/B = 0.72(1)/0.28(1); only atom C27 is affected. Interstitial THF O51/O52 occupies two orientations with populations 0.60(1)/0.40(1), respectively. THF O71 is disordered about a crystallographic threefold axis; this molecule was modeled as a rigid pentagon with 1/3 occupancy. No hydrogen atoms were located or calculated for THF O71. All interstitial atoms were assigned as fixed isotropic displacement parameter of 0.15 Å<sup>2</sup> for refinement stability. These species appear to be fully populated based on trial refinements of site occupancies. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The final absolute structure (Flack) parameter refined to -0.006(11), indicating the correct chiral sense of the crystal and the absence of racemic twinning. All  $L_{ala}$  stereocenters (C13 A-D) were determined by the X-ray refinement to have the "*S*" configuration.

 $[Cu_2(L_{ala})_4(HL_{ala})]$  (2) crystallized as blue rectangular bars. The crystals develop cracks and lose crystallinity within seconds of removal from the mother liquor. The data crystal was coated in inert oil and transferred as rapidly as possible to the cold stream of the diffractometer. Nonetheless, broad diffraction maxima and weak scattering above a 20 value of ca. 45° were observed, due to extensive solvent disorder and moderate crystallinity. The compound crystallizes in the space group  $P2_12_12_1$  as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of one [Cu<sub>2</sub>(L<sub>ala</sub>)<sub>4</sub>(HL<sub>ala</sub>)] polymeric repeating unit and a large interstitial volume of heavily disordered solvent species. Non-hydrogen atoms of the polymeric species were refined with anisotropic displacement parameters; hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. A reasonable position for the charge-balancing proton H3E was located in a difference This atom was subsequently fixed and treated as a riding atom. Most of the map. interstitial electron density was modeled as fractionally occupied methylene chloride; one isolated electron density peak was modeled as a water oxygen. In total, 15 independent methylene chloride molecules were refined, with the aid of C-Cl and Cl-Cl distance restraints. Group occupancies and common group isotropic displacement parameters were refined. No hydrogen atoms were located or calculated for these species. The disordered solvent species were calculated to occupy 2611.2 Å<sup>3</sup> per unit cell, or 31.5% of the total unit cell volume. Because of the extent of disorder, the solvent distribution and composition should be regarded as approximate. This is also the reason for the high R-values and relatively low precision of the structural refinement. The absolute structure (Flack) parameter after the final refinement cycle was 0.02(2), indicating the correct chiral sense of the crystal and the absence of racemic twinning. All  $L_{ala}$  stereocenters (C13 A-E) were determined by the X-ray refinement to have the "*S*" configuration.

 $[Cu_2(L_{ala})_4(py)(THF)]$  (3) formed blue blocklike crystals in the space group  $P2_12_12_1$ , as uniquely determined by examination of the pattern of systematic absences in the intensity data. The asymmetric unit consists of one  $[Cu_2(L_{ala})_4(py)(THF)]$  complex and three disordered solvent molecule positions. The coordinated THF molecule is also disordered equally over two orientations, and was refined with a common oxygen atom site (O17A/B). Three independent solvent regions were modeled as THF molecules (O71 and O81/O82) or THF/hexane (O91/C95-C100), with the aid of fifty geometric restraints. The large displacement parameters and the presence of many residual electron density peaks in the disorder region indicate the approximate nature of the disorder model. The disorder and low crystal quality are the reasons for the high R-factors. All non-hydrogen atoms were refined with anisotropic displacement parameters except for atoms affected by disorder (isotropic). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The absolute structure (Flack) parameter refined to 0.056(16), indicating the correct chiral sense of the crystal and the absence of racemic twinning. All L<sub>ala</sub> stereocenters (C13, C28, C43, C58) were determined by the X-ray refinement to have the "S" configuration.

 $[Cu_2(L_{phg})_4(THF)_2]$  (4) forms greenish-blue crystals in the space group  $P2_1$  as determined by the pattern of systematic absences in the intensity data and by the fixed chirality of the ligands used.. The refinement was hampered by disorder affecting several napthalimide ligands and THF molecules. Though the important general features of the structure are well established, the precision of the derived structural information is low. The disorder is also the reason for the weak observed diffraction and high final R-factors. The asymmetric unit consists of two crystallographically independent  $[Cu_2(L_{phg})_4(THF)_2]$ molecules (Cu1/Cu2 and Cu3/Cu4) and a total of four independent THF molecules of crystallization. The eight independent napthalimide ligands were given identical numbering schemes except for label suffixes A through H. Significant electron density in the vicinity of ligand H was interpreted as two-fold rotational disorder of this entire ligand; the second orientation has suffix I. The phenyl substituents of ligands E and G were also disordered; these disorder groups have label suffixes K and J, respectively. All napthalimide ligand disorder components were refined isotropically with fixed populations of 50%. The napthalimide rings themselves were restrained to be geometrically similar to a well-behaved ring system (ligand A); the phenyl substituents were treated as rigid hexagons. Two of the four non-coordinated THF molecules (O51/O52 and O71/O72) are disordered, and were each modeled in two geometrically restrained orientations with total site occupancies constrained to sum to unity. In total, 442 restraints were used to model the disorder. All non-hydrogen atoms which were not affected by disorder were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The final refined absolute structure (Flack) parameter of 0.003(13) indicating the correct

chiral sense of the crystal and the absence of racemic twinning. All  $L_{phg}$  stereocenters (C13 A-H) were determined by the X-ray refinement to have the "*R*" configuration.

Blue-green rectangular bar-shaped crystals of  $[Cu_4(L_{asn})_8(py)(MeOH)]$  (5) crystallize in the orthorhombic space group  $P2_12_12_1$  as determined by the pattern of systematic absences in the intensity data. The crystallographically identifiable contents of the asymmetric unit consist of one  $[Cu_4(L_{asn})_8(py)(MeOH)]$  molecule, one diethyl ether, two methanol and three dichloromethane molecules. The eight independent ligands of the copper complex were labeled identically except for the label suffix A-H. Solvent species in some regions of the asymmetric unit could not be resolved due to disorder. These were treated as diffusely scattering volumes, and their contributions to the structure factors were removed with the SQUEEZE program implemented in PLATON. These disordered volumes occupy a total of 3973.1 Å<sup>3</sup> (23.2% of the unit cell volume) and account for 1006 e per unit cell. Based on trial disorder modeling attempts, the disordered species are likely a mixture of ether, methanol and dichloromethane. All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon and nitrogen were placed in geometrically idealized positions and included as riding atoms. Reasonable positions for the methanol hydrogens were located in difference maps, and subsequently treated as riding atoms. The final absolute structure (Flack) parameter is 0.044(6), indicating the correct absolute structure and the absence of racemic twinning. All Lasn stereocenters (C13 A-H) were determined by the X-ray refinement to have the "S" configuration.

Blue rectangular bars of  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  (6) crystallize in the space group  $P2_12_12_1$  as determined uniquely by the pattern of systematic absences in the intensity

data. The crystallographically identifiable contents of the asymmetric unit consist of one  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  molecule and three non-coordinated ethyl lactate molecules. The atom numbering scheme is the same as for the MeOH adduct. There is disorder of the -CHCH<sub>2</sub>C(O)NH<sub>2</sub> substituent of ligand "A" that bridges the two dicopper units. The second component of this group has the suffix "Z". This substituent occupies two orientations with equal populations. The pyridine molecule (N3-C25) coordinated to Cu1 is also disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. After identification of the primary  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$ molecule and the three non-coordinated ethyl lactate molecules, a large region of essentially featureless electron density remained in the vicinity of napthalimide rings "B" and "C". This electron density was assumed to be heavily disordered solvent species, probably including more ethyl lactate molecules. No reliable disorder model could be achieved despite many trials, and therefore the program SQUEEZE was used to remove this electron density from subsequent structure factor calculations. The solvent region occupies a volume of 3232.5  $Å^3$ , or 19% of the total unit cell volume. Only the four copper atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. Four napthalimide rings (A, B, C, F) and two non-coordinated ethyl lactate molecules (O56, O66) were each assigned common isotropic displacement parameters. A full anisotropic refinement was not warranted because of the low data quality caused by weak diffraction and disorder. A total of 1351 geometric restraints were employed in the refinement. These were mostly used to maintain reasonable napthalimide geometry, by restraining all napthalimide rings to be similar to ring "G", which was deemed to be

the best-behaved. The disordered -CHCH<sub>2</sub>C(O)NH<sub>2</sub> substituent of ligand "A" was also restrained, and also all three non-coordinated ethyl lactate molecules, which were restrained to have a similar geometry as the coordinated ethyl lactate. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl protons of the four ethyl lactate molecules could not be located and were not calculated. The final absolute structure (Flack) parameter refined to 0.05(2), reliably indicating the correct chiral sense of the crystal and the absence of racemic twinning. Stereocenters in all  $L_{asn}$  ligands (C13 A-H) and in the ethyl lactate molecules (C34, C44, C54 and C64) were determined by the X-ray refinement to have the "S" configuration.

Blue rectangular bars of  $[Cu_4(L_{asn})_8(py)\{(R-EtLac)_{0.58}(MeOH)_{0.42}\}]$  (7) created by exchange with (*R*)- ethyl lactate vapor also crystallize in the space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> as determined uniquely by the pattern of systematic absences in the intensity data. The crystallographically identifiable contents of the asymmetric unit consist of one  $[Cu_4(L_{asn})_8(py)\{(R-EtLac)_{0.58}(MeOH)_{0.42}\}]$  molecule. The atom numbering scheme is the same as for the MeOH adduct. Species coordinated to Cu3 were modeled as disordered ethyl lactate and methanol molecules. Refinement as a fully populated ethyl lactate resulted in unreasonably large displacement parameters for all atoms of the group except the oxygen and carbon closest to Cu3. Refinement as 100% methanol left several large electron density peaks with the general form of an ethyl lactate molecule. For refinement, all atoms of these groups were assigned a common isotropic displacement parameter and their occupancies were constrained to sum to unity. This yielded  $U_{iso} = 0.082(1)$  Å<sup>2</sup> and occupancies of 0.58(1) ethyl lactate and 0.42(1) methanol. The methanol atoms O39 and

C36 were refined with identical x, y, z coordinates as atoms O38 and C34, respectively, of the ethyl lactate molecule. Some C-C and C-O distance restraints were used for these molecules, but none which would affect the stereochemistry (i.e., only directly bonded atoms were restrained). The stereochemistry of the coordinated ethyl lactate (C34) was determined to be "R". The pyridine molecule (N3-C25) coordinated to Cu1 is disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. After identification of the primary  $[Cu_4(L_{asn})_8(py)(R-EtLac)]$  molecule, a largely featureless distribution of electron density remained in the difference maps. No reliable disorder model could be achieved, and therefore the program SQUEEZE was used to remove the contribution of this electron density from the structure factors. The solvent region occupies a volume of 5855.1  $Å^3$ , or 34% of the total unit cell volume. Only the four copper atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. A full anisotropic refinement was not warranted because of the moderate data quality caused by disorder. A total of 995 geometric restraints were employed in the refinement. These were mostly to restrain all naphthalimide ring systems to be similar to "G", which was deemed the best behaved. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl protons of the disordered ethyl lactate and methanol molecule could not be located and were not calculated. The final absolute structure (Flack) parameter refined to 0.089(13), reliably indicating the correct chiral sense of the crystal and its components, and the absence of racemic twinning. All Lasn stereocenters (C13 A-H) were determined by the X-ray refinement to have the "S" configuration.

Blue rectangular bars of  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  (8) created by exchange with racemic ethyl lactate vapor also adopt the space group  $P2_12_12_1$  as determined uniquely by the pattern of systematic absences in the intensity data. Only the  $[Cu_4(L_{asn})_8(py)(S-$ EtLac)] complex could be crystallographically identified; all interstitial species are too severely disordered to impose a physically reasonable disorder model. There is again two-fold disorder of the -CHCH<sub>2</sub>C(O)NH<sub>2</sub> substituent of ligand "A" (atoms C13, C14, C15, N2, O3). The second component of this group has the atom label suffix "Z". The pyridine molecule (atoms N3, C21-C25) coordinated to Cu1 is also disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. The guest region occupies a volume of 5914.7  $Å^3$ , or 34% of the total unit cell volume. All diffusely scattering species in these regions were removed from the structure factor calculations with SQUEEZE. Four naphthalimide ring systems (A, B, C, F), some atoms of rings G and E, and the (S)-ethyl lactate molecule were each assigned common isotropic displacement parameters. Only the four copper atoms were refined anisotropically; all other non-hydrogen atoms were refined isotropically. A full anisotropic refinement was not warranted because of the diminished data quality caused by weak diffraction and disorder. A total of 1041 geometric restraints were employed in the refinement. These were mostly used to maintain reasonable naphthalimide geometry, by restraining all naphthalimide rings to be similar to ring "G", which was deemed to be the most well-behaved. Geometric restraints were also used for the disordered -CHCH<sub>2</sub>C(O)NH<sub>2</sub> substituent of ligand "A" and for the (S)-ethyl lactate molecule (neighboring C-C and C-O distances only; no restraints affecting the chiral sense of the molecule were used). Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl proton of the (*S*)-ethyl lactate molecule could not be located and was not calculated. The final absolute structure (Flack) parameter refined to 0.06(3), reliably indicating the correct chiral sense of the crystal and the absence of racemic twinning. All  $L_{asn}$  stereocenters (C13 A-H) and the ethyl lactate stereocenter (C34) were determined by the X-ray refinement to have the "*S*" configuration.

Blue rectangular bars of  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  (9) formed from both the exchange of 8 with (S)-ethyl lactate and of 7 with racemic ethyl lactate crystallize in the space group  $P2_12_12_1$  as determined uniquely by the pattern of systematic absences in the intensity data. The crystallographically identifiable contents of the asymmetric unit consist of one  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  molecule and one non-coordinated ethyl lactate molecule. The atom numbering scheme is the same as for the MeOH adduct. There is two-fold positional disorder of the naphthalimide ring system of ligand "A". The second component of this group has atom label suffix "Z". The two orientations have nearly equal populations (A/Z = 0.52(1)/0.48(1)). The pyridine molecule (N3-C25) coordinated to Cu1 is also disordered over two equally populated, closely spaced positions (atom label suffixes I and J). These groups were refined as rigid hexagons with a common isotropic displacement parameter. The stereochemistry of the coordinated ethyl lactate (C34) was determined to be "S". After identification of the primary  $[Cu_4(L_{asn})_8(py)(S-$ EtLac)] molecule, one non-coordinated ethyl lactate molecule was clearly located in a difference map. Atoms of this molecule were refined freely (C41-C45, O46-O48), revealing the stereochemistry at atom C44 to be "S". Beyond this interstitial molecule, a

large region of heavily disordered electron density remained. Fragments of ethyl lactate molecules were apparent, but no reliable disorder model could be achieved. Many additional electron density peaks were assumed to be other solvent species. The program SQUEEZE was used to remove the contribution of this electron density from the structure factors. The solvent region occupies a volume of 5503.4 Å<sup>3</sup>, or 31% of the total unit cell volume. Only the four copper atoms were refined anisotropically; all other nonhydrogen atoms were refined isotropically. Disorder component "Z" of napthalimide ring "A" and some atoms of ring "C" were each assigned common isotropic displacement parameters. A full anisotropic refinement was not warranted because of the moderate data quality caused by disorder. A total of 1116 geometric restraints were employed in the refinement. These were mostly to restrain all napthalimide ring systems to be similar to "G", which was deemed the most well-behaved. Some C-C and C-O distance restraints were used for the coordinated and non-coordinated ethyl lactate molecules. No restraints which would affect the stereochemistry were used (i.e., only directly bonded atoms were restrained). Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The hydroxyl protons of the two ethyl lactate molecules could not be located and were not calculated. The final absolute structure (Flack) parameter refined to 0.059(13), reliably indicating the correct chiral sense of the crystal and its components. All  $L_{asn}$  stereocenters (C13 A-H) were determined by the X-ray refinement to have the "S" configuration.

$[Cu_2(L_{ala})_4(THF)_2] (1)$	$[Cu_2(L_{ala})_4(HL_{ala})] (2)$	$[Cu_2(L_{ala})_4(py)(THF)] (3)$						
$C_{87.33}H_{96.67}N_4O_{21.33}Cu_2$	$C_{80.02}H_{51}C_{110.03}N_5O_{20.73}Cu_2$	$C_{82}H_{80}N_5O_{19.50}Cu_2$						
Hexagonal	Orthorhombic	Orthorhombic						
<i>P</i> 63	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$						
25.6612(5)	15.6310(10)	17.7756(12)						
25.6612(5)	16.2439(11)	18.5085(13)						
21.6189(9)	32.635(2)	22.7270(16)						
90	90	90						
90	90	90						
120	90	90						
12328.7(6)	8286.4(10)	7477.2(9)						
6	4	4						
0.44 x 0.40 x 0.34	0.22 x 0.16 x 0.06	0.38 x 0.24 x 0.22						
104024	82477	108015						
14582 [R(int) = 0.0685]	11942 [R(int) = 0.1427]	13308 [R(int) = 0.0798]						
Semi-empirical from equivalents	None	None						
934	1082	908						
1.051	0.954	1.035						
R1 = 0.0535, $wR2 = 0.1391$	R1 = 0.0719, $wR2 = 0.1714$	R1 = 0.0695, $wR2 = 0.1890$						
R1 = 0.0669, wR2 = 0.1495	R1 = 0.1205, wR2 = 0.1912	R1 = 0.0810, $wR2 = 0.1949$						
-0.006(11)	0.02(2)	0.056(16)						
	$\frac{[Cu_{2}(L_{ala})_{4}(THF)_{2}] (1)}{[Cu_{2}(L_{ala})_{4}(THF)_{2}] (1)}$ $C_{87,33}H_{96,67}N_{4}O_{21,33}Cu_{2}$ Hexagonal P63 25.6612(5) 25.6612(5) 21.6189(9) 90 90 120 12328.7(6) 6 0.44 x 0.40 x 0.34 104024 14582 [R(int) = 0.0685] Semi-empirical from equivalents 934 1.051 R1 = 0.0535, wR2 = 0.1391 R1 = 0.0669, wR2 = 0.1495 -0.006(11)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $						

 Table S1.
 Selected crystallographic data for paddlewheel compounds 1-9.

 Table S1. (cont'd)

Compound	$[Cu_2(L_{phg})_4(THF)_2]$ (4)	$[Cu_4(L_{asn})_8(py)(MeOH)]$ (5)	$[Cu_4(L_{asn})_8(py)(S-EtLac)] (6)$
Formula	$C_{96}H_{80}N_4O_{20}Cu_2$	$C_{143}H_{121}Cl_6N_{17}O_{44}Cu_4$	$C_{153}H_{133}N_{17}O_{52}Cu_4$
Crystal System	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a (Å)	15.0013(8)	15.3235(5)	15.1091(8)
b (Å)	23.3563(12)	21.9549(8)	21.4458(12)
c (Á)	23.8248(12)	50.9472(18)	52.381(3)
alpha (deg)	90	90	90
beta (deg)	90.6580(10)	90	90
gamma (deg)	90	90	90
Volume (Å3)	8347.1(7)	17140.0(10)	16972.8(16)
Z	4	4	4
Size (mm3)	0.38 x 0.35 x 0.24	0.50 x 0.35 x 0.18	0.24 x 0.10 x 0.06 mm3
No. of reflens	43700	218466	167453
Indep. Reflens	22082 [R(int) = 0.0430]	30385 [R(int) = 0.0657]	22429 [R(int) = 0.2058]
Abs. Correction	Semi-empirical from equivalents	Semi-empirical from equivalents	None
Parameters	1969	1932	850
GOF	1.045	1.041	0.846
Final R [I>2sigma(I)]	R1 = 0.0678, $wR2 = 0.1838$	R1 = 0.0433, $wR2 = 0.1007$	R1 = 0.0866, wR2 = 0.1940
R (all data)	R1 = 0.0873, $wR2 = 0.2014$	R1 = 0.0510, $wR2 = 0.1038$	R1 = 0.1534, $wR2 = 0.2220$
Abs. Structure Parameter	0.003(13)	0.044(6)	0.05(2)

## Table S1. (cont'd)

$[Cu_{4}(L_{asn})_{8}(py) \{(R-EtLac)_{0.58(1)}(MeOH)_{0.42(1)}\}] (7)$ $C_{136.32}H_{100.48}N_{17}O_{42.16}Cu_{4}$	$[Cu_{4}(L_{asn})_{8}(py)(S-EtLac)] (8)$ $C_{138}H_{103}N_{17}O_{43}Cu_{4}$	$[Cu_{4}(L_{asn})_{8}(py)(S-EtLac)] (9)$ $C_{143}H_{113}N_{17}O_{46}Cu_{4}$
Orthorhombic	Orthorhombic	Orthorhombic
$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
15.250(2)	15.1728(15)	15.2568(11)
21.548(3)	21.670(2)	21.8967(16)
52.359(7)	52.697(5)	52.720(4)
90	90	90
90	90	90
90	90	90
17206(4)	17327(3)	17612(2)
4	4	4
0.44 x 0.22 x 0.20	0.20 x 0.08 x 0.06	0.54 x 0.24 x 0.22
232763	75115	236144
27766 [R(int) = 0.1064]	11917 [ $R(int) = 0.2005$ ]	28085 [R(int) = 0.0830]
Semi-empirical from equivalents	None	Semi-empirical from equivalents
787	742	853
1.044	0.879	1.021
R1 = 0.0800, wR2 = 0.2106	R1 = 0.0782, wR2 = 0.1660	R1 = 0.0796, $wR2 = 0.2061$
R1 = 0.0979, $wR2 = 0.2215$	R1 = 0.1232, $wR2 = 0.1814$	R1 = 0.0884, $wR2 = 0.2128$
0.089(13)	0.06(3)	0.059(13)
	$[Cu_4(L_{asn})_8(py)\{(R-EtLac)_{0.58(1)}(MeOH)_{0.42(1)}\}] (7)$ $C_{136.32}H_{100.48}N_{17}O_{42.16}Cu_4$ Orthorhombic $P2_12_12_1$ $15.250(2)$ $21.548(3)$ $52.359(7)$ $90$ $90$ $90$ $90$ $17206(4)$ $4$ $0.44 \times 0.22 \times 0.20$ $232763$ $27766 [R(int) = 0.1064]$ Semi-empirical from equivalents $787$ $1.044$ $R1 = 0.0800, wR2 = 0.2106$ $R1 = 0.0979, wR2 = 0.2215$ $0.089(13)$	$ \begin{bmatrix} Cu_4(L_{asn})_8(py) \{ (R-EtLac)_{0.58(1)}(MeOH)_{0.42(1)} \} \end{bmatrix} (7) \\ C_{136,32}H_{100,48}N_{17}O_{42,16}Cu_4 \\ Orthorhombic \\ P2_12_12_1 \\ 15.250(2) \\ 21.548(3) \\ 21.548(3) \\ 21.670(2) \\ 52.359(7) \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 90 \\ 9$

	$[Cu_2(L_{ala})_4(THF)_2]$	$[Cu_2(L_{ala})_4(HL_{ala})]$	$[Cu_2(L_{ala})_4]$	$[Cu_2(\mathbf{L_{phg}})_4(THF)_2]$	$[Cu_2(\mathbf{L_{phg}})_4(THF)_2]$	
	(1)	(2)	(py)(THF)] ( <b>3</b> )	( <b>4</b> , ABCD)	( <b>4</b> , EFG(H/I))	
Cu(1)…Cu(2)	2.6018(6)	2.6165(15)	2.6270(8)	2.6213(11)	2.6201(13)	Cu(3)…Cu(4)
Cu(1)-O(3A)	1.945(3)	1.989(6)	1.931(4)	1.985(5)	1.942(5)	Cu(3)-O(3E)
Cu(1)-O(3B)	1.972(3)	1.936(7)	2.023(4)	1.927(5)	1.937(7)	Cu(3)-O(3F)
Cu(1)-O(3C)	1.949(3)	1.956(7)	1.941(4)	2.014(5)	1.951(5)	Cu(3)-O(3G)
Cu(1)-O(3D)	1.992(3)	1.944(7)	2.002(4)	1.932(5)	1.852(10)/2.032(11)	Cu(3)-O(3H/I)
Cu(2)-O(4A)	1.960(3)	1.976(6)	2.011(4)	1.935(5)	1.953(5)	Cu(4)-O(4E)
Cu(2)-O(4B)	1.936(3)	1.930(6)	1.917(4)	1.966(5)	1.941(6)	Cu(4)-O(4F)
Cu(2)-O(4C)	1.961(3)	1.932(8)	2.006(4)	1.926(5)	1.953(5)	Cu(4)-O(4G)
Cu(2)-O(4D)	1.933(3)	1.941(7)	1.896(4)	1.966(5)	1.914(10)/1.961(10)	Cu(4)-O(4H/I)
Cu(2)-La	2.203(3)	2.278(7)	2.183(4)	2.214(5)	2.219(6)	Cu(4)- Lα
Cu(1)-Lβ	2.219(3)	2.227(6)	2.185(4)	2.158(5)	2.163(6)	$Cu(3)$ -L $\beta$
	$[Cu_4(\mathbf{L}_{asn})_8 (py)(MeOH)] $ (1)	$\begin{bmatrix} Cu_4(L_{asn})_8 & [Cu_4(L_{asn})_8] \\ (py)(S-EtLac) & (py)(S-EtLac) \end{bmatrix} $	$\begin{array}{ll} _{4}(\mathbf{L}_{asn})_{8} & [Cu_{4}\\ S-EtLac)] & (py)(\mathbf{M}\\ EFGH) & (5 \ F\end{array}$	( <b>L</b> <sub>asn</sub> ) <sub>8</sub> MeOH)] EFGH)		
	Cu(1)…Cu(2) Cu(1)-O(3A) Cu(1)-O(3B) Cu(1)-O(3C) Cu(1)-O(3D) Cu(2)-O(4A) Cu(2)-O(4B) Cu(2)-O(4C) Cu(2)-O(4D) Cu(2)-Lα Cu(1)-Lβ	$\begin{array}{c} [{\rm Cu}_2({\rm L}_{ala})_4({\rm THF})_2] \\ (1) \\ (1) \\ (1) \\ (1) \\ (1) \\ (2$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

**Table S2.** Selected distances for paddlewheel compounds 1-9. For compound 4, the right hand labeling scheme refers to molecule EFGH/I. For compounds 5-9, the right hand labeling scheme refers to the two columns to the right.

		$[Cu_4(L_{asn})_8 (py)(MeOH)]$ (5, ABCD)	$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (6, ABCD)$	[Cu <sub>4</sub> (L <sub>asn</sub> ) <sub>8</sub> (py)(S-EtLac)] ( <b>6</b> , EFGH)	$[Cu_4(L_{asn})_8 (py)(MeOH)]$ (5, EFGH)	
Equatorial	Cu(1)…Cu(2)	2.7185(5)	2.712(2)	2.6088(19)	2.6714(5)	Cu(3)-Cu(4)
	Cu(1)-O(4A)	1.944(2)	1.918(8)	1.962(8)	1.950(2)	Cu(3)-O(4E)
	Cu(1)-O(4B)	2.033(2)	2.008(8)	1.982(8)	2.015(2)	Cu(3)-O(4F)
	Cu(1)-O(4C)	1.930(2)	1.910(8)	1.939(7)	1.952(2)	Cu(3)-O(4G)
	Cu(1)-O(4D)	2.075(2)	2.071(8)	1.967(8)	1.974(2)	Cu(3)-O(4H)
	Cu(2)-O(5A)	2.026(2)	2.034(8)	2.018(8)	2.021(2)	Cu(4)-O(5E)
	Cu(2)-O(5B)	1.896(2)	1.910(8)	1.935(8)	1.965(2)	Cu(4)-O(5F)
	Cu(2)-O(5C)	2.002(2)	2.013(8)	2.016(8)	1.993(2)	Cu(4)-O(5G)
	Cu(2)-O(5D)	1.923(2)	1.908(9)	1.967(7)	1.944(2)	Cu(4)-O(5H)
Axial α	Cu(1)-N(3I)	2.143(3)	2.143(10)	2.246(9) (O36)	2.163(2)	Cu(3)-O(6)
Axial β	Cu(2)-O(3E)	2.130(2)	2.129(10)	2.125(9)	2.142(2)	Cu(4)-O(3A)

		$[Cu_4(L_{asn})_8(py) \{(R-EtLac)_{0.58(1)}(MeOH)_{0.42(1)}\}]$ (7, ABCD)	[Cu <sub>4</sub> (L <sub>asn</sub> ) <sub>8</sub> (py)(S-EtLac)] (8, ABCD)	$[Cu_4(L_{asn})_8(py) \{(R-EtLac)_{0.58(1)}(MeOH)_{0.42(1)}\}]$ (7, EFGH)	[Cu <sub>4</sub> (L <sub>asn</sub> ) <sub>8</sub> (py)(S-EtLac)] (8, EFGH)	
Equatorial	Cu(1)-Cu(2)	2.7207(10)	2.692(3)	2.6171(11)	2.606(3)	Cu(3)-Cu(4)
	Cu(1)-O(4A)	1.915(5)	1.928(12)	1.959(4)	1.993(11)	Cu(3)-O(4E)
	Cu(1)-O(4B)	2.017(4)	2.020(11)	1.993(4)	1.946(10)	Cu(3)-O(4F)
	Cu(1)-O(4C)	1.929(5)	1.905(12)	1.955(5)	1.943(11)	Cu(3)-O(4G)
	Cu(1)-O(4D)	2.035(5)	2.039(12)	1.969(5)	1.993(11)	Cu(3)-O(4H)
	Cu(2)-O(5A)	2.046(4)	2.003(13)	1.974(4)	1.984(11)	Cu(4)-O(5E)
	Cu(2)-O(5B)	1.911(4)	1.870(11)	1.959(4)	1.934(10)	Cu(4)-O(5F)
	Cu(2)-O(5C)	1.991(5)	1.975(12)	1.980(5)	2.018(11)	Cu(4)-O(5G)
	Cu(2)-O(5D)	1.905(5)	1.899(13)	1.954(4)	1.929(10)	Cu(4)-O(5H)
Axial α	Cu(1)-N(3I)	2.180(7)	2.177(12)	2.203(7)	2.242(16)	Cu(3)-O(36)/O(38)
Axial β	Cu(2)-O(3E)	2.115(5)	2.064(13)	2.137(5)	2.136(13)	Cu(4)-O(3A)

		$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (9, ABCD)$	$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (9, EFGH)$	
Equatorial	Cu(1)-Cu(2)	2.6720(10)	2.6241(10)	Cu(3)-Cu(4)
-	Cu(1)-O(4A)	1.961(5)	1.981(4)	Cu(3)-O(4E)
	Cu(1)-O(4B)	2.019(4)	1.967(4)	Cu(3)-O(4F)
	Cu(1)-O(4C)	1.937(5)	1.971(5)	Cu(3)-O(4G)
	Cu(1)-O(4D)	2.021(5)	1.941(4)	Cu(3)-O(4H)
	Cu(2)-O(5A)	2.007(4)	2.004(4)	Cu(4)-O(5E)
	Cu(2)-O(5B)	1.916(4)	1.961(4)	Cu(4)-O(5F)
	Cu(2)-O(5C)	1.998(5)	1.968(4)	Cu(4)-O(5G)
	Cu(2)-O(5D)	1.943(5)	1.975(4)	Cu(4)-O(5H)
Axial α	Cu(1)-N(3I)	2.170(6)	2.215(3)	Cu(3)-O(36)
Axial β	Cu(2)-O(3E)	2.118(4)	2.151(5)	Cu(4)-O(3A)

		$[Cu_2(L_{ala})_4(THF)_2]$	$[Cu_2(L_{ala})_4$	$[Cu_2(L_{ala})_4$	$[Cu_2(\mathbf{L_{phg}})_4(THF)_2]$	$[Cu_2(L_{phg})_4(THF)_2]$	
		(1)	$(HL_{ala})]$ (2)	(py)(THF)] ( <b>3</b> )	( <b>4</b> , ABCD)	( <b>4</b> , EFG(H/I))	
Equatorial	O(3A)-Cu(1)-Cu(2)	83.49(9)	87.91(18)	87.89(11)	79.51(14)	88.03(17)	O(3E)- $Cu(3)$ - $Cu(4)$
	O(3B)-Cu(1)-Cu(2)	81.11(9)	82.40(19)	81.25(12)	83.04(15)	88.42(17)	O(3F)-Cu(3)-Cu(4)
	O(3C)-Cu(1)-Cu(2)	89.41(9)	84.0(2)	86.73(12)	84.87(14)	83.49(16)	O(3G)-Cu(3)-Cu(4)
	O(3D)-Cu(1)-Cu(2)	84.54(8)	84.9(2)	84.03(12)	88.71(15)	81.6(4)/72.1(4)	O(3H/I)-Cu(3)- Cu(4)
	O(4A)-Cu(2)-Cu(1)	85.98(9)	81.76(18)	81.26(11)	89.85(15)	80.50(16)	O(4E)-Cu(4)-Cu(3)
	O(4B)-Cu(2)-Cu(1)	88.45(9)	87.3(2)	87.67(12)	85.73(14)	80.31(16)	O(4F)-Cu(4)-Cu(3)
	O(4C)-Cu(2)-Cu(1)	79.96(9)	85.1(2)	81.75(11)	83.61(14)	85.19(15)	O(4G)- $Cu(4)$ - $Cu(3)$
	O(4D)-Cu(2)-Cu(1)	85.03(9)	84.2(2)	84.51(12)	79.91(14)	86.6(4)/95.7(4)	O(4H/I)-Cu(4)- Cu(3)
	O(3A)-Cu(1)-O(3B)	89.59(14)	91.8(3)	89.30(18)	91.3(2)	90.7(3)	O(3E)-Cu(3)-O(3F)
	O(3A)-Cu(1)-O(3C)	172.88(13)	171.7(3)	174.63(17)	164.3(2)	171.5(2)	O(3E)-Cu(3)- O(3G)
	O(3A)-Cu(1)-O(3D)	89.75(13)	89.4(3)	89.40(17)	88.8(2)	93.0(6)/84.7(5)	O(3E)-Cu(3)-O(3H/I)
	O(3B)-Cu(1)-O(3C)	88.77(14)	88.9(3)	89.93(18)	87.9(2)	89.6(3)	O(3F)-Cu(3)-O(3G)
	O(3B)-Cu(1)-O(3D)	165.62(12)	167.2(3)	165.26(17)	171.6(2)	169.2(5)/160.1(5)	O(3F)-Cu(3)-O(3H/I)
	O(3C)-Cu(1)-O(3D)	90.13(13)	88.1(3)	90.00(18)	89.7(2)	85.3(6)/92.2(5)	O(3G)-Cu(3)-O(3H/I)
	O(4A)-Cu(2)-O(4B)	90.10(13)	88.9(3)	88.67(18)	90.6(2)	90.6(2)	O(3E)-Cu(4)-O(3F)
	O(4A)-Cu(2)-O(4C)	165.88(13)	166.6(3)	162.72(16)	173.4(2)	165.4(2)	O(3E)-Cu(4)- O(3G)
	O(4A)-Cu(2)-O(4D)	88.80(13)	90.0(3)	90.62(17)	91.0(2)	90.9(5)/86.6(5)	O(3E)-Cu(4)- O(3H/I)
	O(4B)-Cu(2)-O(4C)	90.81(13)	87.9(3)	87.50(18)	87.8(2)	89.9(2)	O(3E)-Cu(3)-O(3H/I)
	O(4B)-Cu(2)-O(4D)	173.45(12)	171.5(3)	172.16(17)	165.5(2)	166.4(5)/175.5(4)	O(3F)-Cu(4)-O(3G)
	O(4C)-Cu(2)-O(4D)	88.69(13)	91.3(3)	90.88(17)	89.0(2)	85.2(5)/91.9(5)	O(3G)-Cu(4)-O(3H/I)
Axial α	$L\alpha$ -Cu(2)-Cu(1)	170.97(9)	165.59(17)	177.54(14)	167.53(14)	163.05(15)	$L\alpha$ -Cu(4)-Cu(3)
	O(4A)-Cu(2)-Lα	101.23(12)	84.6(2)	99.94(17)	93.03(19)	88.1(2)	$O(4E)$ - $Cu(4)$ -L $\alpha$
	O(4B)-Cu(2)-Lα	96.89(12)	87.9(3)	94.50(17)	106.4(2)	87.4(2)	O(4F)- $Cu(4)$ -La
	O(4C)- $Cu(2)$ -La	92.64(12)	108.3(3)	97.16(17)	93.61(19)	106.5(2)	O(4G)-Cu(4)-Lα
	O(4D)-Cu(2)-Lα	89.66(12)	100.4(3)	93.31(17)	87.9(2)	106.2(5)/96.0(5)	O(4H/I)-Cu(4)-Lα
Axial β	$L\beta$ -Cu(1)-Cu(2)	170.34(9)	173.34(18)	177.31(13)	170.65(16)	169.5(2)	$L\beta$ -Cu(3)-Cu(4)
·	$O(3A)$ - $Cu(1)$ - $L\beta$	91.43(13)	89.4(2)	92.87(16)	91.9(2)	92.3(2)	O(3E)-Cu(3)-Lβ
	$O(3B)$ - $Cu(1)$ - $L\beta$	90.67(13)	91.6(3)	96.17(17)	93.5(2)	102.1(3)	O(3F)-Cu(3)-Lβ
	O(3C)-Cu(1)-Lβ	95.52(13)	98.8(3)	92.51(17)	103.7(2)	95.9(2)	O(3G)-Cu(3)-Lβ

**Table S3.** Selected bond angles for paddlewheel compounds 1-9. For compound 4, the right hand labeling scheme refers to molecule EFGH/I. For compounds 5-9, the right hand labeling scheme relates to the two columns to the right.

	O(3D)-Cu(1)-Lβ	103.71(12)	101.1(3)	98.55(17)	94.9(2)	87.9(5)/97.4(5))
		$[Cu_4(L_{asn})_8 (py)(MeOH)] (5, ABCD)$	$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (6, ABCD)$	$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (6, EFGH)$	$[Cu_4(L_{asn})_8 (py)(MeOH)] (5, EFGH)$	
Equatorial	O(4A)-Cu(1)-Cu(2)	88.36(7)	89.3(3)	91.4(2)	91.61(6)	O(4E)-Cu(3)-Cu(4)
	O(4B)-Cu(1)-Cu(2)	76.75(6)	79.2(2)	79.9(2)	77.44(6)	O(4F)-Cu(3)-Cu(4)
	O(4C)-Cu(1)-Cu(2)	87.87(7)	86.3(2)	84.1(2)	82.76(6)	O(4G)-Cu(3)-Cu(4)
	O(4D)-Cu(1)-Cu(2)	77.52(7)	78.0(2)	86.0(2)	84.80(7)	O(4H)-Cu(3)-Cu(4)
	O(5A)-Cu(2)-Cu(1)	78.07(6)	77.3(2)	78.3(2)	76.12(6)	O(5E)-Cu(4)-Cu(3)
	O(5B)-Cu(2)-Cu(1)	89.66(7)	87.7(2)	88.1(2)	90.44(6)	O(5F)-Cu(4)-Cu(3)
	O(5C)-Cu(2)-Cu(1)	78.43(7)	79.3(2)	84.6(2)	84.51(6)	O(5G)-Cu(4)-Cu(3)
	O(5D)-Cu(2)-Cu(1)	88.90(7)	88.1(3)	83.8(2)	82.68(7)	O(5H)-Cu(4)-Cu(3)
	O(4A)-Cu(1)-O(4B)	90.06(9)	91.4(3)	89.0(3)	89.33(9)	O(4E)-Cu(3)-O(4F)
	O(4A)-Cu(1)-O(4C)	176.06(9)	174.7(3)	173.8(3)	172.36(10)	O(4E)-Cu(3)-O(4G)
	O(4A)-Cu(1)-O(4D)	87.87(9)	86.4(3)	85.8(3)	86.35(10)	O(4E)-Cu(3)-O(4H)
	O(4B)-Cu(1)-O(4C)	90.20(9)	90.6(3)	94.5(3)	94.45(9)	O(4G)-Cu(3)-O(4F)
	O(4B)-Cu(1)-O(4D)	154.24(9)	157.2(3)	164.8(3)	161.60(9)	O(4H)-Cu(3)-O(4F)
	O(4C)-Cu(1)-O(4D)	90.18(9)	89.8(3)	89.6(3)	87.99(10)	O(4G)-Cu(3)-O(4H)
	O(5A)-Cu(2)-O(5B)	88.06(10)	88.6(3)	84.8(3)	85.79(9)	O(5F)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5C)	156.47(9)	156.5(3)	162.9(3)	160.61(9)	O(5G)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5D)	89.77(10)	89.8(3)	90.4(3)	90.21(9)	O(5H)-Cu(4)-O(5E)
	O(5B)-Cu(2)-O(5C)	92.97(10)	93.4(3)	94.8(3)	93.52(9)	O(5F)-Cu(4)-O(5G)
	O(5B)-Cu(2)-O(5D)	177.61(10)	175.7(3)	171.2(3)	172.71(10)	O(5H)-Cu(4)-O(5F)
	O(5C)-Cu(2)-O(5D)	88.62(10)	86.5(3)	87.6(3)	88.22(10)	O(5H)-Cu(4)-O(5G)
Axial α	N(3I)-Cu(1)-Cu(2)	175.96(8)	173.0(5)	167.3(3)	168.36(8) (O(6))	O(36)-Cu(3)-Cu(4)
	O(4A)-Cu(1)-N(3I)	91.61(10)	87.2(6)	91.4(3)	90.74(10) (O(6))	O(4E)-Cu(3)-O(36)
	O(4B)-Cu(1)-N(3I)	99.20(10)	94.8(7)	87.8(3)	91.19(10) (O(6))	O(4F)-Cu(3)-O(36)
	O(4C)-Cu(1)-N(3I)	92.23(10)	97.5(5)	93.9(3)	95.81(9) (O(6))	O(4G)-Cu(3)-O(36)
	O(4D)-Cu(1)-N(3I)	106.52(11)	107.7(7)	106.6(3)	106.73(10) (O(6))	O(4H)-Cu(3)-O(36)
Axial β	O(3E)-Cu(2)-Cu(1)	176.11(7)	175.8(3)	172.9(4)	172.24(7)	O(3A)-Cu(4)-Cu(3)
	O(5A)-Cu(2)-O(3E)	98.49(9)	99.0(3)	94.7(5)	96.80(9)	O(5E)-Cu(4)-O(3A)
	O(5B)-Cu(2)-O(3E)	88.40(10)	90.3(3)	92.3(5)	92.21(9)	O(5F)-Cu(4)-O(3A)

O(3H/I)-Cu(1)-Lβ

	O(5C)-Cu(2)-O(3E)	105.04(9)	104.4(3)	102.4(5)	) 102.59(9)	O(5G)-Cu(4)-O(3A)	
	O(5D)-Cu(2)-O(3E)	92.92(9)	93.9(4)	95.3(5)	94.32(10)	O(5H)-Cu(4)-O(3A)	
							_
		[Cu <sub>4</sub> (L <sub>asn</sub> ) <sub>8</sub> (py)	{( <i>R</i> -		$[Cu_4(L_{asn})_8(py)\{(R-$		
		EtLac) <sub>0.58(1)</sub> (MeOH	$[)_{0.42(1)}\}$	$[Cu_4(L_{asn})_8]$	EtLac) <sub>0.58(1)</sub> (MeOH) <sub>0.42(1)</sub>	$[Cu_4(L_{asn})_8]$	
		]		(py)(S-EtLac)]	]	(py)(S-EtLac)]	
		(7, ABCD)		( <b>8</b> , ABCD)	(7, EFGH)	( <b>8</b> , EFGH)	
Equatorial	O(4A)-Cu(1)-Cu(2)	90.10(14)		88.3(4)	88.65(13)	91.3(3)	O(4E)-Cu(3)-Cu(4)
	O(4B)- $Cu(1)$ - $Cu(2)$	78.76(12)		78.7(3)	80.32(12)	81.7(3)	O(4F)-Cu(3)-Cu(4)
	O(4C)-Cu(1)-Cu(2)	86.01(14)		86.9(4)	83.80(13)	82.8(3)	O(4G)- $Cu(3)$ - $Cu(4)$
	O(4D)-Cu(1)-Cu(2)	78.64(16)		77.1(3)	84.86(13)	86.2(3)	O(4H)- $Cu(3)$ - $Cu(4)$
	O(5A)-Cu(2)-Cu(1)	76.29(12)		78.9(4)	80.86(13)	79.3(3)	O(5E)-Cu(4)-Cu(3)
	O(5B)-Cu(2)-Cu(1)	87.65(12)		87.3(3)	88.28(12)	87.6(3)	O(5F)-Cu(4)-Cu(3)
	O(5C)-Cu(2)-Cu(1)	79.69(13)		80.0(3)	85.18(13)	85.2(3)	O(5G)-Cu(4)-Cu(3)
	O(5D)-Cu(2)-Cu(1)	89.07(14)		87.7(4)	83.59(13)	83.2(3)	O(5H)-Cu(4)-Cu(3)
	O(4A)-Cu(1)-O(4B)	90.31(19)		90.1(5)	90.78(17)	89.6(4)	O(4E)-Cu(3)-O(4F)
	O(4A)-Cu(1)-O(4C)	176.0(2)		174.8(5)	170.45(19)	172.5(5)	O(4E)-Cu(3)-O(4G)
	O(4A)-Cu(1)-O(4D)	87.74(19)		87.1(5)	86.49(19)	85.7(4)	O(4E)-Cu(3)-O(4H)
	O(4B)-Cu(1)-O(4C)	89.79(18)		91.0(5)	93.70(18)	94.1(4)	O(4G)-Cu(3)-O(4F)
	O(4B)-Cu(1)-O(4D)	156.32(18)		155.8(4)	164.99(18)	166.9(5)	O(4H)-Cu(3)-O(4F)
	O(4C)-Cu(1)-O(4D)	90.57(19)		89.8(5)	87.00(19)	89.3(4)	O(4G)-Cu(3)-O(4H)
	O(5A)-Cu(2)-O(5B)	87.57(17)		89.8(5)	86.41(17)	84.7(4)	O(5F)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5C)	155.96(18)		158.6(5)	165.89(19)	164.5(4)	O(5G)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5D)	89.82(19)		87.8(5)	88.92(19)	89.9(4)	O(5H)-Cu(4)-O(5E)
	O(5B)-Cu(2)-O(5C)	92.32(18)		92.9(5)	95.21(18)	94.4(4)	O(5F)-Cu(4)-O(5G)
	O(5B)-Cu(2)-O(5D)	176.22(19)		174.8(5)	171.17(18)	170.1(4)	O(5H)-Cu(4)-O(5F)
	O(5C)-Cu(2)-O(5D)	88.9(2)		87.7(5)	87.53(18)	88.6(4)	O(5H)-Cu(4)-O(5G)
Axial α	N(3I)-Cu(1)-Cu(2)	175.9(4)		174.0(8)	171.03(18)	169.4(4)	O(36)/O(38)-Cu(3)-Cu(4)
	O(4A)-Cu(1)-N(3I)	89.2(4)		88.9(8)	91.4(2)	93.3(5)	O(4E)-Cu(3)-O(36)/O(38)
	O(4B)-Cu(1)-N(3I)	97.2(4)		96.0(10)	90.7(2)	88.8(5)	O(4F)-Cu(3)-O(36)/O(38)
	O(4C)-Cu(1)-N(3I)	94.8(4)		96.0(8)	96.9(2)	93.2(5)	O(4G)-Cu(3)-O(36)/O(38)
	O(4D)-Cu(1)-N(3I)	106.4(4)		108.0(10)	104.1(2)	103.6(5)	O(4H)-Cu(3)-O(36)/O(38)
Axial β	O(3E)-Cu(2)-Cu(1)	170.00(15)		174.4(4)	177.80(15)	169.7(7)	O(3A)-Cu(4)-Cu(3)
,	O(5A)-Cu(2)-O(3E)	93.88(19)		95.9(5)	98.17(19)	90.7(7)	O(5E)-Cu(4)-O(3A)

	O(5B)-Cu(2)-O(3E)	93.79(19)	90.8(5)	89.70(18)
	O(5C)-Cu(2)-O(3E)	110.1(2)	105.3(5)	95.85(19)
	O(5D)-Cu(2)-O(3E)	89.1(2)	94.0(5)	98.4(2)
		$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (9, ABCD)$	$[Cu_4(L_{asn})_8 (py)(S-EtLac)] (9, EFGH)$	
Equatorial	O(4A)-Cu(1)-Cu(2)	88.62(14)	90.77(12)	O(4E)-Cu(3)-Cu(4)
1	O(4B)-Cu(1)-Cu(2)	80.89(12)	81.48(12)	O(4F)-Cu(3)-Cu(4)
	O(4C)-Cu(1)-Cu(2)	86.57(13)	82.92(13)	O(4G)-Cu(3)-Cu(4)
	O(4D)-Cu(1)-Cu(2)	78.20(13)	88.08(13)	O(4H)-Cu(3)-Cu(4)
	O(5A)-Cu(2)-Cu(1)	79.61(12)	78.51(11)	O(5E)-Cu(4)-Cu(3)
	O(5B)-Cu(2)-Cu(1)	86.68(13)	87.52(11)	O(5F)-Cu(4)-Cu(3)
	O(5C)-Cu(2)-Cu(1)	81.65(14)	86.19(12)	O(5G)-Cu(4)-Cu(3)
	O(5D)-Cu(2)-Cu(1)	89.59(14)	81.58(13)	O(5H)-Cu(4)-Cu(3)
	O(4A)-Cu(1)-O(4B)	90.82(19)	89.29(17)	O(4E)-Cu(3)-O(4F)
	O(4A)-Cu(1)-O(4C)	175.1(2)	172.02(18)	O(4E)-Cu(3)-O(4G)
	O(4A)-Cu(1)-O(4D)	88.58(19)	86.78(18)	O(4E)-Cu(3)-O(4H)
	O(4B)-Cu(1)-O(4C)	89.39(18)	94.57(18)	O(4G)-Cu(3)-O(4F)
	O(4B)-Cu(1)-O(4D)	159.09(18)	168.79(18)	O(4H)-Cu(3)-O(4F)
	O(4C)-Cu(1)-O(4D)	89.47(19)	88.13(19)	O(4G)-Cu(3)-O(4H)
	O(5A)-Cu(2)-O(5B)	89.24(19)	86.32(16)	O(5F)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5C)	161.21(18)	164.69(17)	O(5G)-Cu(4)-O(5E)
	O(5A)-Cu(2)-O(5D)	90.43(19)	90.47(17)	O(5H)-Cu(4)-O(5E)
	O(5B)-Cu(2)-O(5C)	91.11(19)	92.52(17)	O(5F)-Cu(4)-O(5G)
	O(5B)-Cu(2)-O(5D)	176.26(19)	169.04(17)	O(5H)-Cu(4)-O(5F)
	O(5C)-Cu(2)-O(5D)	87.99(19)	87.82(17)	O(5H)-Cu(4)-O(5G)
Axial α	N(3I)-Cu(1)-Cu(2)	176.0(3)	169.43(12)	O(36)-Cu(3)-Cu(4)
	O(4A)-Cu(1)-N(3I)	90.9(3)	90.24(17)	O(4E)-Cu(3)-O(36)
	O(4B)-Cu(1)-N(3I)	95.2(3)	88.01(17)	O(4F)-Cu(3)-O(36)
	O(4C)-Cu(1)-N(3I)	94.0(3)	96.86(17)	O(4G)-Cu(3)-O(36)
	O(4D)-Cu(1)-N(3I)	105.7(3)	102.48(17)	O(4H)-Cu(3)-O(36)
Axial β	O(3E)-Cu(2)-Cu(1)	171.15(12)	170.18(14)	O(3A)-Cu(4)-Cu(3)
	O(5A)-Cu(2)-O(3E)	92.88(17)	93.02(18)	O(5E)-Cu(4)-O(3A)

<sup>94.1(7)</sup>O(5F)-Cu(4)-O(3A)104.8(7)O(5G)-Cu(4)-O(3A)94.3(8)O(5H)-Cu(4)-O(3A)

O(5B)-Cu(2)-O(3E)	88.55(17)	96.98(17)	O(5F)-Cu(4)-O(3A)
O(5C)-Cu(2)-O(3E)	105.91(18)	102.26(18)	O(5G)-Cu(4)-O(3A)
O(5D)-Cu(2)-O(3E)	95.19(18)	93.64(19)	O(5H)-Cu(4)-O(3A)



**Figure S1.** Partially numbered ellipsoid diagram of the repeating unit of  $[Cu_2(L_{ala})_4(HL_{ala})]$  (2). Displacement ellipsoids drawn at the 30% probability level. \* indicates a symmetry-equivalent atom. Atoms of the five ligands numbered identically except for label suffix A through E. Only ligand "C" is labeled fully; the other ligands follow the same labeling pattern.



**Figure S2.** Partially numbered diagram of  $[Cu_2(L_{ala})_4(py)(THF)]$  (3). Displacement ellipsoids drawn at the 30% probability level. Only ring "A" is fully labeled; the rings B – D follow the same labeling pattern. Hydrogen atoms omitted and only the major disordered orientation of the THF ligand is shown.









# (d)

**Figure S3.** Displacement ellipsoid / sphere plots of the two crystallographically independent molecules in  $[Cu_2(L_{phg})_4(THF)_2]$  (4). Only one naphthalimide ligand is fully labeled; the others follow the same labeling pattern. (a) Cu1/Cu2 and ligands A-D molecule. Displacement ellipsoids drawn at the 30% probability level. (b) Ball-and-stick plot of Cu3/Cu4 and ligands E-I. Disorder of ligand H/I and disorder of phenyl rings G/J and E/K shown. (c) Cu3/Cu4 and ligand EFGH disorder component. Displacement ellipsoids drawn at the 20% probability level. (d) Cu3/Cu4 and ligand EFGI disorder component. Displacement ellipsoids drawn at the 20% probability level.



Figure S4. Partially numbered ellipsoid plot of  $[Cu_4(L_{asn})_8(py)(MeOH)]$  (5). Displacement ellipsoids drawn at the 30% probability level.



**Figure S5.**  $[Cu_4(L_{asn})_8(py)(S-EtLac)]$  (6). Displacement ellipsoids (Cu) and spheres drawn at the 20% probability level. Ligand "G" labeled fully; the other follow the same pattern. Hydrogen atoms omitted for clarity. Disorder of ligand "A" (-CHCH<sub>2</sub>C(O)NH<sub>2</sub>) components A/Z shown. Interstitial molecules omitted.

### Additional supramolecular structural analysis of [Cu<sub>2</sub>(L<sub>phg</sub>)<sub>4</sub>(THF)<sub>2</sub>] (4)

The ABCD dimer also has a phenyl-naphthalimide  $\pi - \pi$  stacking interaction, shown in Figure S6. This interaction is substantially weaker than the naphthalimide-naphthalimide stacking interaction, as evidenced by the long phenyl centroid to naphthalimide arene centroid distance (4.40 Å).



**Figure S6.** ABCD phenyl-naphthalimide stacking interactions in the structure of **4**, viewed from the  $\beta$ -face. Phenyl rings shown in blue, stacking interactions indicated by magenta dotted lines.

The EFGH ring system has a similar interaction, which is shown in Figure S7. In this system, the phenyl-naphthalimide  $\pi \cdots \pi$  stacking interaction is joined by an edge-to-face naphthalimidenaphthalimide interaction, the first interaction of this type observed in our work. The  $\pi \cdots \pi$  interaction is slightly stronger than that seen for the other dimer, with a centroid-centroid distance of 4.0 Å. The CH $\cdots \pi$  interactions are reasonably strong, with H $\cdots$ centroid distances of 3.09 and 3.85 Å, and C-H $\cdots$ centroid angles of 168° and 166°.



**Figure S7.** EFGH  $\pi$ -- $\pi$  and CH-- $\pi$  interactions, viewed from the  $\beta$ -face in the structure of 4. E, F, and G phenyl rings shown in green, H phenyl ring in red. Blue dotted lined indicate the interactions.

In the EFGI dimer, the phenyl-naphthalimide  $\pi - \pi$  interaction has been replaced by a naphthalimide-naphthalimide  $\pi - \pi$  interaction, due to the inverted configuration of ring I (Figure S8). This interaction is strong, with a reasonable vertical separation (3.51 Å), and a very low  $\chi$  (0.61 Å). The naphthalimide-naphthalimide vectors are oriented nearly head-to-tail, with an angle of 175°. The rings are also almost coplanar, with an angle of only 3.5°.



**Figure S8.** EFGI  $\pi \cdots \pi$  stacking interactions. E, F, and G phenyl rings shown in green, I phenyl ring in red.