Supplementary Information

Trinuclear Cu^{II} Complex with Functionalized s-Heptazine N-ligands: Molecular Chemistry from a g-C_3N_4 fragment

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Table of Contents **pag.**

Description Synthesis of 1-5

General procedure

All reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. The reaction at 550ºC was performed in a Nabertherm P330 furnace. For the synthesis of **4** an Anton Paar Monowave 300 microwave reactor was employed.

Infrared spectra (4000−400 cm−1) were recorded on a Bruker IFS- 125 FT-IR spectrophotometer. The analysis of C, H, N and S were performed with a Perkin-Elmer 2400 series II analyzer. NMR spectra were collected at r.t. on a Varian Mercury 400 spectrometer. ^{1}H NMR spectra were referenced *vs* TMS as internal standard. Fluorescence studies of ligand **4** and complex $[Cu_3Cl_3(L)_2](ClO_4)_3$ (**5**) were performed Fluorimetro Nanolog^{TM} Horib Jobin Yvon IHR320.

X-ray diffraction experiment was performed on a Bruker-AXS Kappa Mach3 APEX-II diffractometer with INCOATEC Helios mirrors at 100K with a rotating Mo-anode source. Compound **5** crystallizes with several molecules of dichloromethane and methanol of which three CH_2Cl_2 molecules per trinuclear complex unit were found to be well defined whereas four CH_2Cl_2 and four methanol molecules per formula unit were detected to be severely disordered in channels parallel to the crystallographic a-axis. These contributions were removed using the program Platon-SQUEEZE since no satisfactory disorder model could be refined, (Platon program suite, A.L.Spek, Acta Cryst. 2009, D65, 148-155.)

Synthesis of polymeric melon (hydrogenated g-C_3N_4, 1). The synthesis was done following the procedure previously reported[1] also we have follow some of the procedures described by the PhD thesis of Andreas Sattler, München University, 2010 (http://edoc.ub.uni-muenchen.de/11666/1/Sattler_Andreas.pdf). Urea (70g, 1.17 mol) was put into a crucible and dried at 120 ºC during 24h. The crucible was covered and heated at 550 ºC during 3h. 3.4g of a light yellow solid were obtained. FT-IR (KBr pellets, ν / cm^{-1}): 3300-3000, 1638s, 1573m, 1537m, 1461s, 1407s, 1316s, 1238s, 1208m, 814w.

Synthesis of $C_6N_7O_3K_3$ (2,5,8-tris(potassium)cyamelurate, 2). Following a previously reported procedure[2] a suspension of **1** (3.7g) in 100 ml of 2M $KOH_{(aq)}$ was heated to reflux during 4 h. The obtained clear solution was filtered and let to allow room temperature. Ethanol was added to the solution and a white solid appears. It was filtered, washed with ethanol and dried at 55ºC 24h to yield 3.38g (10 mmol). FT-IR (KBr pellets, ν / cm^{-1}): 1635m, 1576s, 1521s, 1413s, 1157w, 816m.

Synthesis of $C_6N_7Cl_3$ (cyameluric chloride, 3). Following a previously reported procedure[2] [S2] a mixture of **2** (2.4g, 7.2 mmol) and PCl_5 (4.4g, 21.1 mmol) were intimately mixed and placed into a Schlenk flask under N_2. It was heated at 130 ºC during 16 h. The Schlenk flask was opened several times to release the generated overpressure. The obtained yellow solid can be purified either by sublimation under reduced pressure at 330

ºC, after 48h a yield of 5% was obtained (100 mg, 0.36 mmol) or Soxhlet extraction with toluene gives a yield of 16% . FT-IR (KBr pellets, ν / cm^{-1}): 1652s, 1609s, 1506m, 1306s, 1204s, 1088w, 942m, 824m, 649w.

Synthesis of $C_6N_7(N(C_5NH_4)_2)_3$ (2,5,8-tris(di-2-pyridinylamine)-s-heptazine, 4). Into a 30 ml glass tube was placed **3** (152 mg, 0.54 mmol), 2.2'-dipyridylamine (554 mg, 3.23 mmol), 15 ml of anhydrous toluene was added and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. The mixture was heated under microwave irradiation at 220 ºC during 4 min with constant stirring of 600 rpm. The conditions of the reaction under microwave irradiation are showed in Figure S1. The obtained white solid was filtrated and washed several times with acetone. The solid was suspended in 200 ml of acetone using an ultrasonic bath and filtrated to yield 67% (250mg, 1.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.37 (dd, 1H, J_1=4.7 Hz), 7.71 (m, 1H), 8.2 (d, 1H, J=8.2 Hz), 7.13 (ddd, 1H, J_1=7.4 Hz, J_2=4.7 Hz, J_3=1.0 Hz); Anal. Calcd (found) for $C_6N_7(N(C_5NH_4)_2)_3$: C, 63.5 (61.3); H, 3.5 (3.4); N, 32.9 (31.7). FT-IR (KBr pellets, ν / cm^{-1}): 3100-3000, 1645s, 1591m, 1446m, 1425s, 1272m, 1152w, 997w, 808w, 780w, 745w, 723w, 607w.

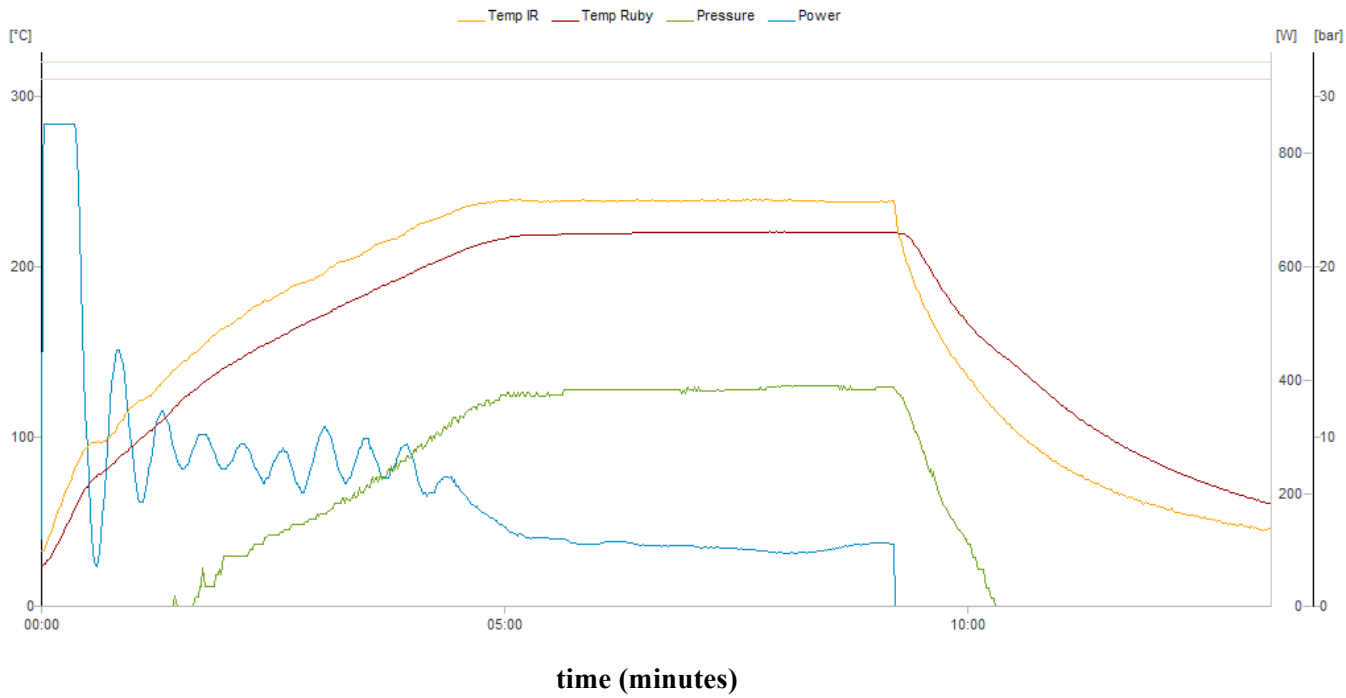


Figure S1. Details of the microwave reaction employed to synthetize **4**. The temperature controlled by IR and Ruby detectors, the pressure and the power are showed in orange, red, green and blue, respectively.

Synthesis of $\{Cu_3[C_6N_7(N(C_5NH_4)_2)_3]_2Cl_3\}(ClO_4)_3 \cdot 3CH_2Cl_2 \cdot$ unknown solvate (5). Ligand **4** (20mg, 29 μmol) was dissolved in 80 ml of MeOH:CH_2Cl_2 (1:1) and a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (8mg, 22 μmol) and $CuCl_2 \cdot 2H_2O$ (4mg, 30 μmol) in 20 ml of MeOH was added dropwise during 1h with slow and constant stirring. The solution was stirred during 10 min. Very slow evaporation gives to blue crystals of **5** after 3 weeks. Anal. Calcd (found) for $[Cu_3Cl_3(L)_2](ClO_4)_3$: C, 40.7 (40.6); H, 2.4 (2.6); N, 20.2 (20.4). FT-IR (KBr pellets, ν / cm^{-1}): 3100-3000, 1645s, 1455m, 1404s, 1285w, 1262w, 1087w, 809w, 624w, 587w.

Table S1. Comparison of the IR peaks of the C_6N_7 moiety in the five synthesized compounds were recorded on a Bruker IFS- 125 FT-IR spectrophotometer.

Compound	**1**	**2**	**3**	**4**	**5**
δ $C_6N_{7\ unit}$	812	819	824,7 81	812, 778, 745	813
ν $C_6N_{7\ unit}$	1635, 1575	1653, 1521	1610, 1505	1635, 1590	1645, 1404
	1411	1413	1307	1406	

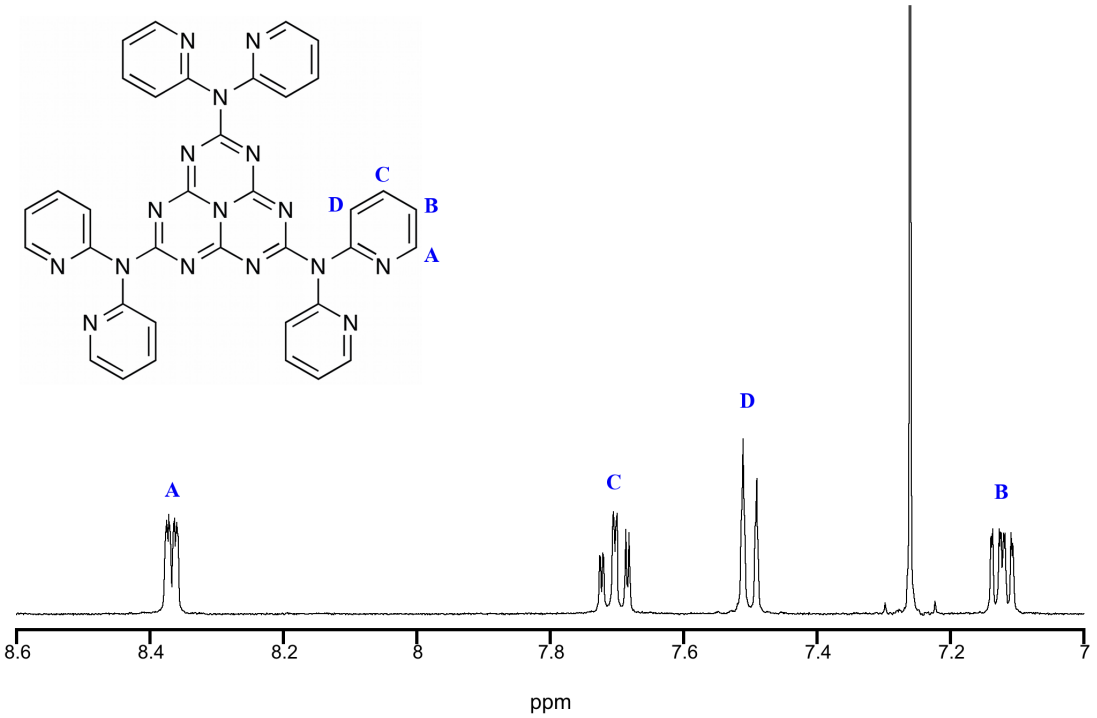
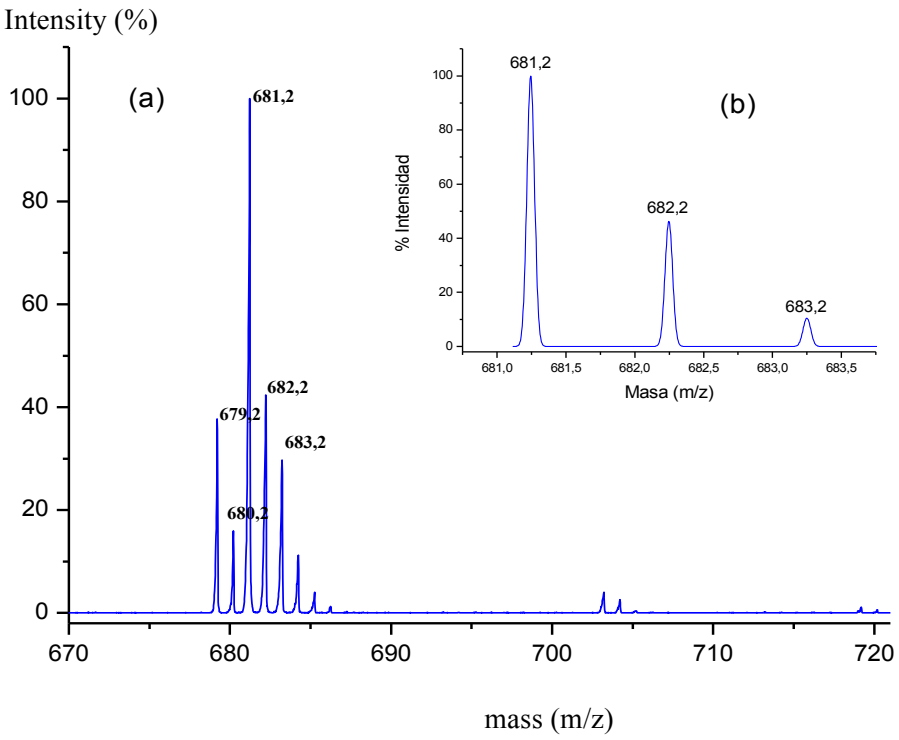


Figure S2. 1H NMR spectrum corresponding to the ligand **4** collected at r.t. on Varian Mercury 400 apparatus. ^{1}H NMR spectra were reference to TMS as internal standard.



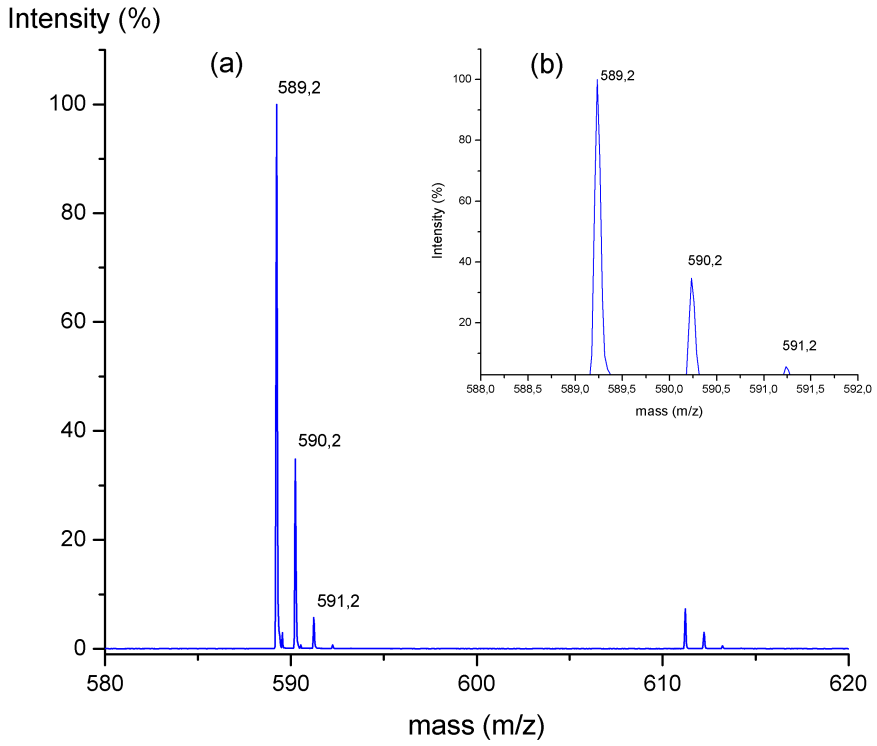


Figure S3. Mass spectra of ligand **4** (above) in CH_2Cl_2/CH_3OH, m/z 681.2 $[M+H]^+$ (a) and calculated (b) and the equivalent triazine ligand (below) in CH_2Cl_2/CH_3OH, m/z 589.2 $[M+H]^+$ (a) and calculated (b). Electrospray ESI-TOF (Agilent Technologies).

Magnetic measurements were carried out using a Quantum Design MPMS SQUID magnetometer. Analysis was performed on crushed polycrystalline samples of compound **5** $[Cu_3Cl_3(L)_2](ClO_4)_3$ (see Figure S4a). The χ T product is almost constant to a value of 1.25 emu-mol^{-1}K in the whole range of temperatures. For three non-interacting Cu^{II} centers a χ T value of 1.125 emu-mol^{-1}K must be obtained, giving for **5** a reasonable g value of 2.22 for such system. Figure S4b χ_M versus T dependence indicate the possible exictence of antiferromagnetic intermolecular interactions with a Curie-Weiss θ parameter of -0.467.

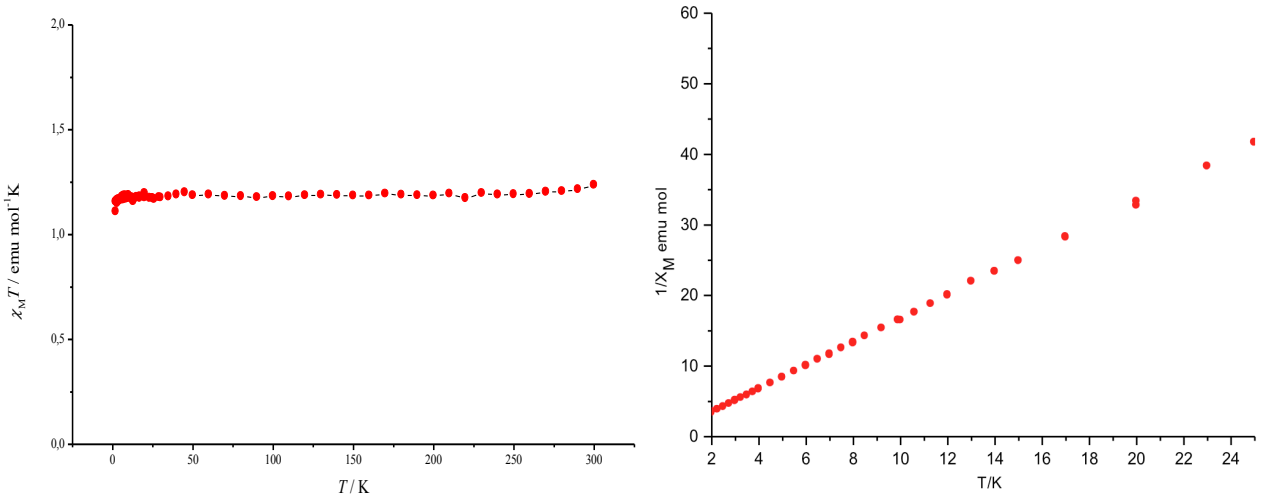


Figure S4. a) χ_M T versus T y (b) 1/χ_M versus T for the complex **5**. Magnetic measurements were carried out using a Quantum Design MPMS SQUID magnetometer.

In order to verify such magnetic behavior DFT calculations using the Gaussian code[3] with the B3LYP functional[4] and a all-electron triple-ζ basis set proposed by Schäefer and coworkers.[5] Three spin configurations were calculated, the S = 3/2 high-spin case (all the spins are parallel) and two S=1/2 solutions (inversion of the spin of the one or the two non-equivalent Cu^{II} centers). The three calculated energies are identical for these spin configuration indicating that the exchange interaction between the Cu^{II} centers is negligible. This fact can be corroborated for the plot of the spin density (see Figure S5) with the three "magnetic orbitals" are almost perpendicular to the heptazine bridging ligand. The spin density distribution also reveals the expected predominance of a delocalization mechanism of the Cu^{II} spin density in the coordinated nitrogen atoms (same sign of the spin density). Furthermore, a spin polarization dominates the spin density distribution in the pyridine ring, as clearly detected by an alternation of the sign of the spin density. The lack of spin density in the heptazine moieties confirm that their orbitals are not mixed with those of the metal in agreement with the negligible exchange coupling between the Cu^{II} centers.

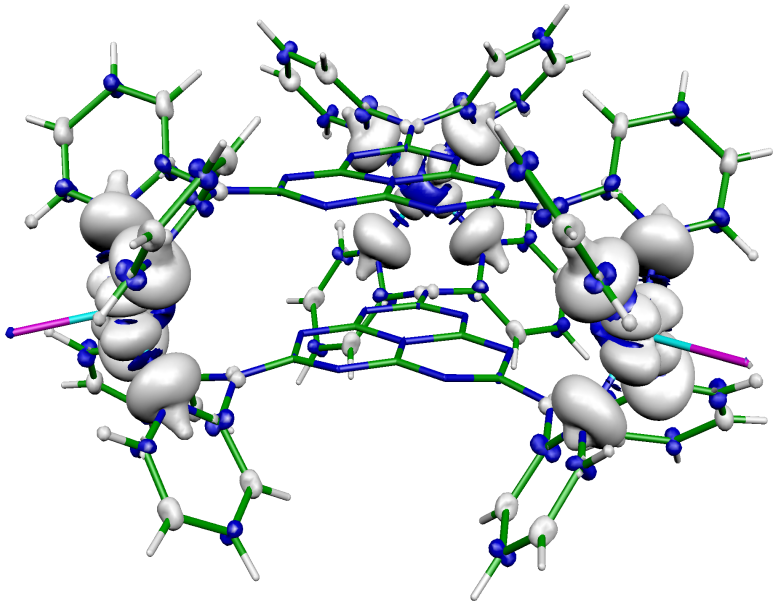


Figure S5. Calculated spin density using the B3LYP functional and all electron triple zeta basis set with the Gaussian09 code for the complex 5 $[Cu_3Cl_3L_2](ClO_4)_3$. The system behaves like three isolated Cu^{II} centers, the d_{x2-y2} orbitals bearing the unpaired electrons are perpendicular to the bridging heptazine ligand. The calculated exchange coupling constant with the same theoretical gives a negligible value.

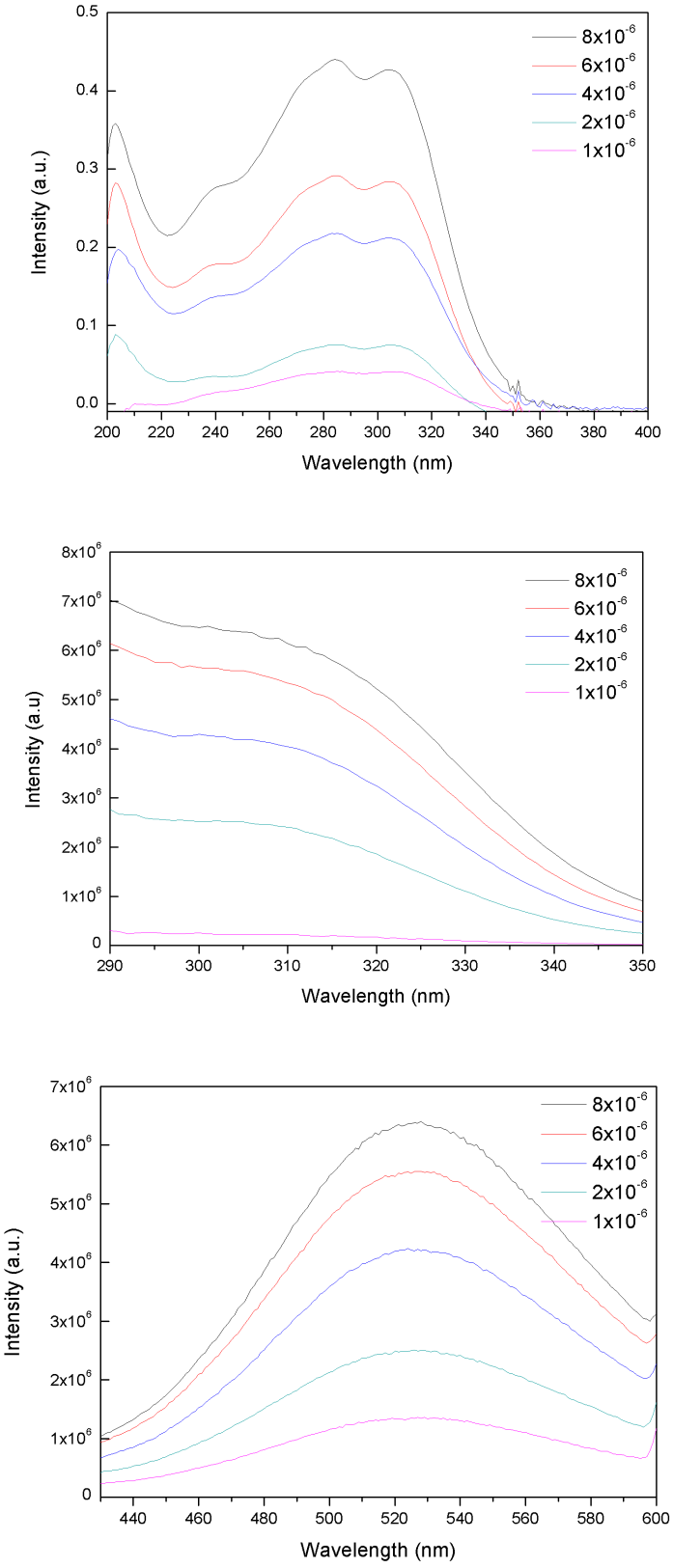
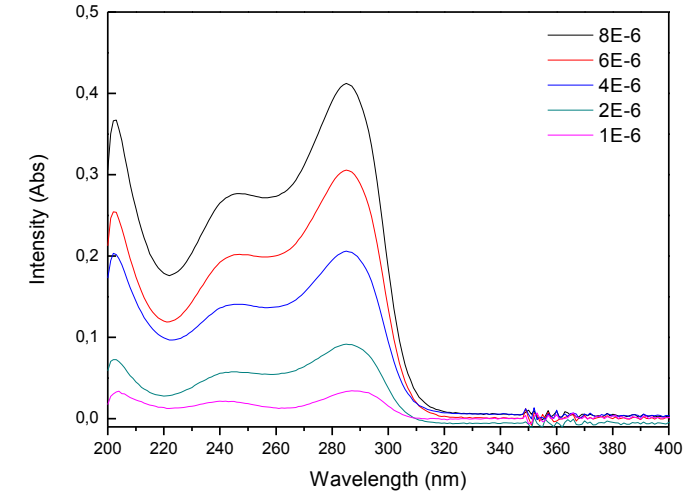
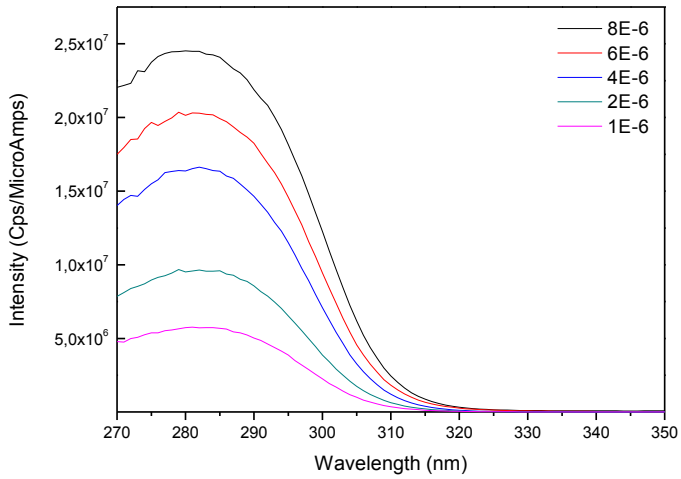


Figure S6. Absorption (above), Excitation (middle) and Emission Spectra (below, using an irradiation of 305 nm) of ligand **4** for different concentration values.





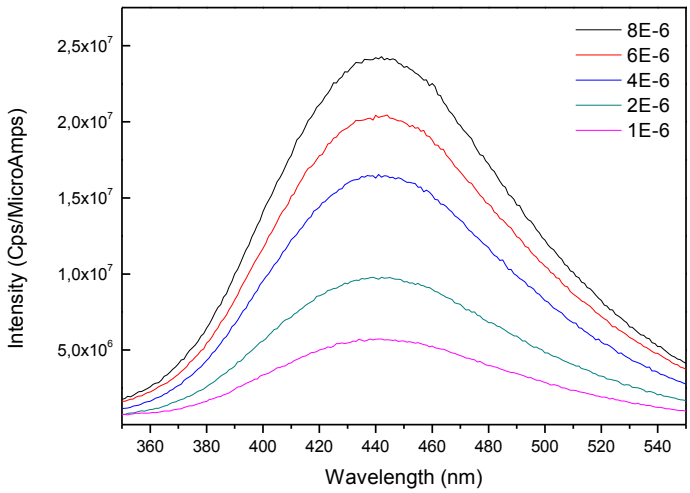


Figure S7. Absorption (above), Excitation (middle) and Emission Spectra (below, using an irradiation of 285 nm) of the equivalent triazine-base ligand (2,4,6-tris(di-2-pyrildilamine)-1,3,5-triazine) for different concentration values.

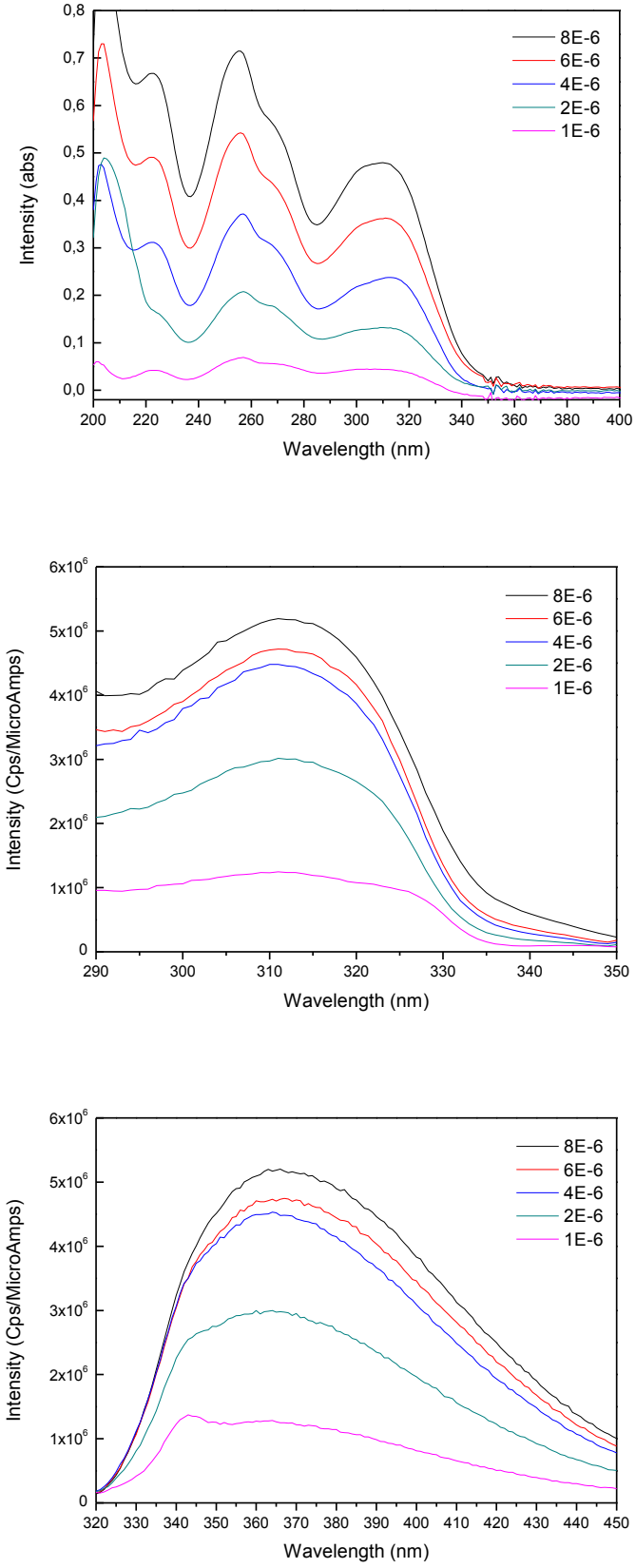


Figure S8. Absorption (above), Excitation (middle) and Emission Spectra (below, using an irradiation of 309 nm) of complex **5** for different concentration values.

TDDFT calculations of ligand 4. To analyze the absorption spectrum of the ligand **4** computational methods have been employed. For the calculation of the excitation energy and oscillator strength, using the Gaussian 09 program[3] with the TDDFT method and the exchange correlation functional PBE1PBE (also called PBE0)[6] together with a 6-311+G** basis set. To simulate the solvent effect a CPCM model was employed. According to these results electronic transitions that appear with greater intensity are produced from HOMO to LUMO orbitals-1 and the LUMO HOMO (see Figure S9) with calculated values of 312 and 313 nm, respectively next to the experimental value of 310 nm (see Figures 4 and S6). It is observed that the transitions between the dipyridylamine HOMO and HOMO-1 orbitals while the LUMO is mainly centered in the heptacine moiety, showing an intramolecular charge transfer for this transition.

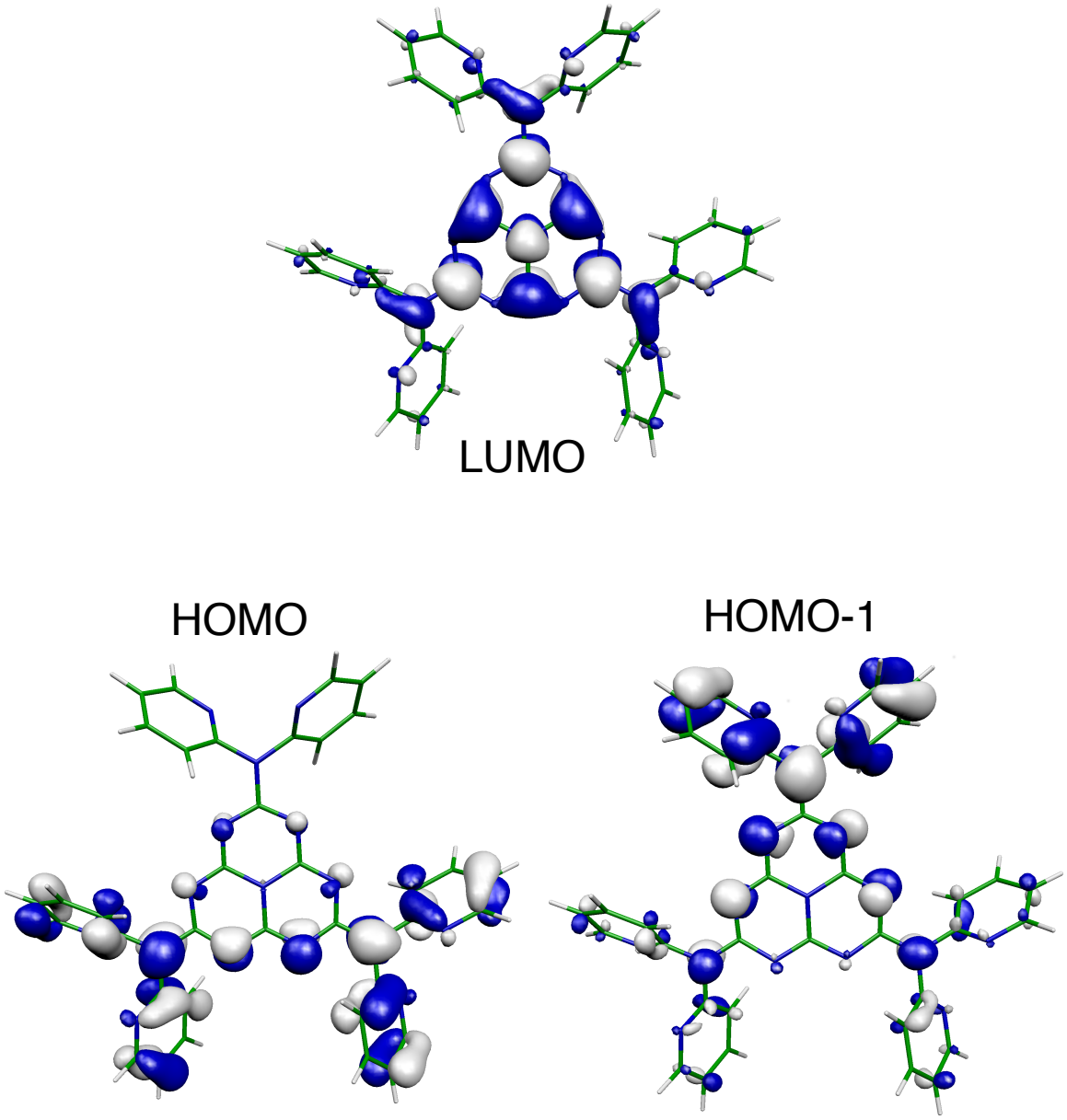


Figure S9. HOMO, HOMO-1 and LUMO orbitals of ligand **4**.

Table S2. Crystal data and structure refinement for complex **5**.

Identification code	9192	
Empirical formula	C_{75} H_{54} Cl_{12} Cu_3 N_{32} O_{12}	
Formula weight	2211.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2/c, No.13	
Unit cell dimensions	a = 28.203(3) Å	α= 90°.
	b = 15.868(2) Å	β= 115.652(2)°.
	c = 25.367(3) Å	γ = 90°.
Volume	10233(2) $Å^3$	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	1.000 mm^{-1}	
F(000)	4460	
Crystal size	0.171 x 0.071 x 0.051 mm^3	
Theta range for data collection	1.513 to 26.000°.	
Index ranges	-34<=h<=34, -19<=k<=19, -31<=l<=31	
Reflections collected	208682	
Independent reflections	20111 [R(int) = 0.1032]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.96086 and 0.89405	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20111 / 87 / 1230	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0743, wR2 = 0.1902	
R indices (all data)	R1 = 0.1105, wR2 = 0.2145	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.165 and -1.300 e.$Å^{-3}$	

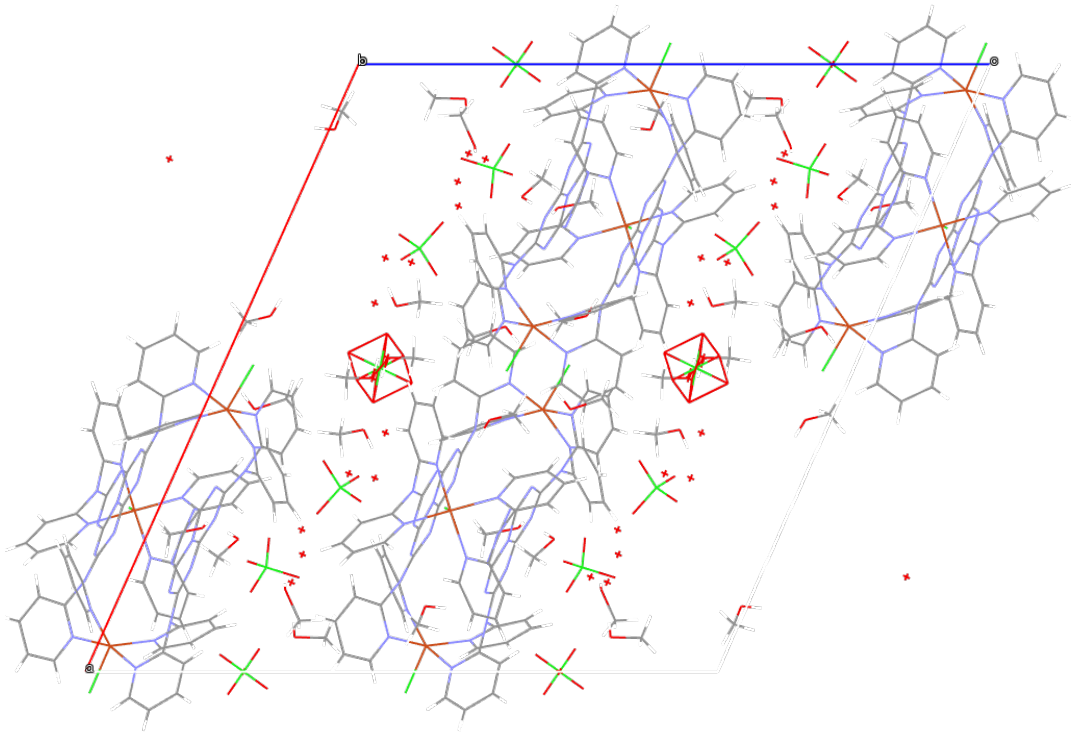


Figure S10. Crystal packing diagram of complex **5** along the *b* axis of the unit cell.

The complex **5** shows an intramolecular π ⋯ π contact[7-9] between the two heptazine moieties as well as a strong anion (ClO_4-)⋯π intermolecular interaction.[10]

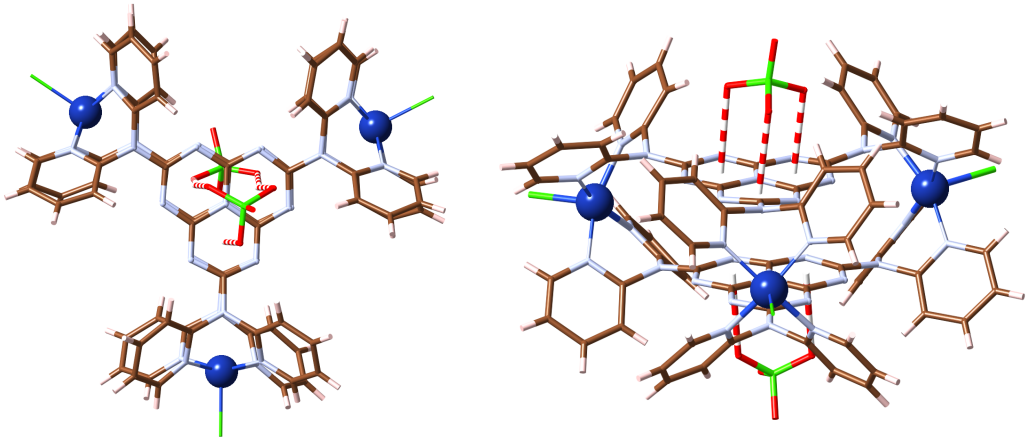


Figure S11. Different views of the structure of complex **5** showing, as dashed bonds, the intermolecular contacts between the outer $[ClO_4]^-$ ions and the heptazines. Copper, chlorine, oxygen, nitrogen, carbon and hydrogen atoms are represented in blue, green, red, light blue, brown and white respectively.

Table S3. Intermolecular contacts between the outer $[ClO_4]^-$ ions and the heptazines. The label $[ClO_4]$_1 corresponds to the perchlorate anion that has three close contacts (see Fig. S11) while the $[ClO_4]$_2 one is that with two close contacts.

	d(O⋯centroid C_3N_3) / Å	d(O⋯C) / Å	d(O⋯N) / Å
$[ClO_4]$_1	2.687	2.840, 2.959, 3.135	3.114, 2.947, 3.026
$[ClO_4]$_1	2.817	3.167, 2.916, 3.219	3.227, 3.124, 3.091
$[ClO_4]$_1	2.949	3.269, 3.176, 3.234	3.365, 3.250, 3.171
$[ClO_4]$_2	2.858	3.269, 3.162, 3.001	3.193, 3.218, 3.117
$[ClO_4]$_2	2.829	3.206, 3.123, 3.030	3.148, 3.185, 3.116
	d(Cl⋯centroidC_3N_3)/Å	d(Cl⋯C)/Å	d(Cl⋯N)/Å
$[ClO_4]$_1	3.313	3.506, 3.604, 3.998	3.313, 3.929, 3.994
$[ClO_4]$_2	3.784	3.641, 4.187, 4,232	3.917, 4.440, 3.784

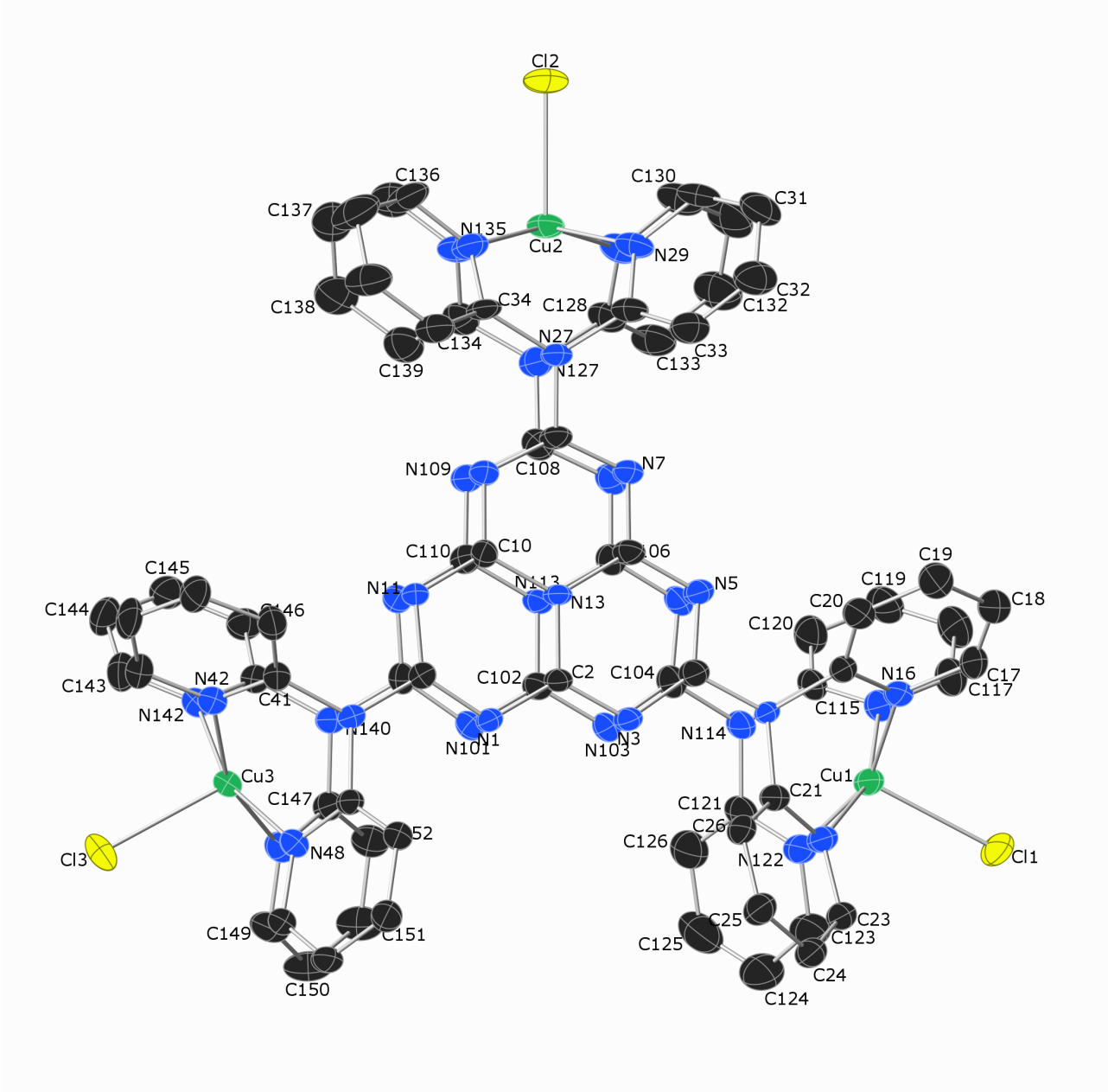


Figure S12. Structure of complex **5** with the labels for identification of the crystallographic data.

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for complex **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	9499(1)	2942(1)	5264(1)	36(1)
Cu(2)	7330(1)	-2743(1)	4596(1)	31(1)
Cu(3)	5781(1)	2953(1)	5399(1)	26(1)
Cl(1)	10264(1)	3644(1)	5296(1)	50(1)
Cl(2)	7225(1)	-4209(1)	4347(1)	48(1)
Cl(3)	5089(1)	3650(1)	5528(1)	41(1)
N(1)	6859(2)	2545(3)	4445(2)	24(1)
C(2)	7242(2)	2136(3)	4386(2)	23(1)
N(3)	7669(2)	2534(3)	4426(2)	27(1)
C(4)	8027(2)	2064(3)	4352(3)	30(1)
N(5)	8036(2)	1220(3)	4296(2)	32(1)
C(6)	7603(2)	819(3)	4241(2)	26(1)
N(7)	7559(2)	-3(3)	4143(2)	28(1)
C(8)	7096(2)	-342(3)	4059(2)	25(1)
N(9)	6697(2)	21(3)	4119(2)	25(1)
C(10)	6741(2)	845(3)	4223(2)	21(1)
N(11)	6359(2)	1263(3)	4286(2)	22(1)
C(12)	6437(2)	2095(3)	4380(2)	22(1)
N(13)	7195(2)	1263(2)	4278(2)	21(1)
N(14)	8455(2)	2477(3)	4356(2)	32(1)
C(15)	8828(2)	2062(4)	4192(3)	36(2)
N(16)	9333(2)	2214(3)	4557(3)	37(1)
C(17)	9705(2)	1923(4)	4404(3)	43(2)
C(18)	9582(3)	1476(4)	3900(4)	53(2)
C(19)	9058(3)	1311(4)	3532(4)	50(2)
C(20)	8674(3)	1620(4)	3680(3)	45(2)
C(21)	8474(2)	3389(4)	4327(3)	35(1)
N(22)	8937(2)	3718(3)	4702(3)	37(1)
C(23)	9015(2)	4546(4)	4652(3)	41(2)
C(24)	8635(2)	5052(4)	4260(3)	42(2)
C(25)	8154(2)	4701(4)	3887(3)	39(2)
C(26)	8074(2)	3849(4)	3923(3)	36(2)
N(27)	7028(2)	-1171(3)	3894(2)	26(1)
C(28)	7384(2)	-1602(3)	3729(3)	30(1)
N(29)	7543(2)	-2361(3)	3974(2)	32(1)
C(30)	7836(3)	-2842(4)	3789(3)	40(2)
C(31)	7991(3)	-2576(4)	3374(3)	45(2)
C(32)	7831(3)	-1773(4)	3132(3)	46(2)
C(33)	7523(3)	-1289(4)	3301(3)	37(1)
C(34)	6543(2)	-1611(3)	3769(3)	28(1)
N(35)	6600(2)	-2356(3)	4029(2)	33(1)
C(36)	6172(3)	-2834(4)	3897(3)	42(2)
C(37)	5681(3)	-2570(4)	3533(4)	57(2)
C(38)	5620(3)	-1776(4)	3273(3)	46(2)
C(39)	6061(2)	-1295(4)	3384(3)	34(1)
N(40)	6035(2)	2522(3)	4423(2)	24(1)
C(41)	5534(2)	2138(3)	4290(2)	26(1)
N(42)	5345(2)	2282(3)	4682(2)	28(1)

C(43)	4854(2)	2011(4)	4554(3)	35(1)
C(44)	4553(2)	1599(4)	4054(3)	38(2)
C(45)	4742(2)	1457(4)	3646(3)	35(1)
C(46)	5251(2)	1725(4)	3767(3)	32(1)
C(47)	6022(2)	3425(3)	4434(2)	24(1)
N(48)	5883(2)	3749(3)	4830(2)	26(1)
C(49)	5791(2)	4586(3)	4809(3)	29(1)
C(50)	5855(2)	5104(3)	4414(3)	31(1)
C(51)	6012(2)	4756(4)	4012(3)	32(1)
C(52)	6091(2)	3904(3)	4015(3)	28(1)
N(101)	7483(2)	2169(3)	5935(2)	28(1)
C(102)	7861(2)	1764(3)	5878(2)	26(1)
N(103)	8291(2)	2179(3)	5934(2)	32(1)
C(104)	8673(2)	1698(4)	5918(3)	33(1)
N(105)	8664(2)	876(3)	5797(2)	34(1)
C(106)	8239(2)	461(4)	5733(3)	31(1)
N(107)	8198(2)	-362(3)	5632(2)	33(1)
C(108)	7761(2)	-721(4)	5609(3)	30(1)
N(109)	7328(2)	-353(3)	5591(2)	28(1)
C(110)	7366(2)	471(3)	5704(2)	25(1)
N(111)	6983(2)	881(3)	5756(2)	24(1)
C(112)	7085(2)	1674(3)	5923(2)	23(1)
N(113)	7821(2)	898(3)	5773(2)	25(1)
N(114)	9138(2)	2115(3)	6041(3)	37(1)
C(115)	9605(2)	1661(4)	6122(3)	36(1)
N(116)	9846(2)	1972(3)	5815(3)	40(1)
C(117)	10318(2)	1638(4)	5909(3)	47(2)
C(118)	10538(3)	997(4)	6288(3)	48(2)
C(119)	10285(2)	672(4)	6605(3)	45(2)
C(120)	9799(2)	1017(4)	6518(3)	42(2)
C(121)	9227(2)	2979(4)	6239(3)	40(2)
N(122)	9433(2)	3452(3)	5966(3)	43(1)
C(123)	9581(3)	4251(4)	6164(4)	55(2)
C(124)	9524(3)	4562(5)	6632(4)	64(2)
C(125)	9303(3)	4069(5)	6902(4)	64(2)
C(126)	9152(3)	3244(5)	6713(4)	52(2)
N(127)	7747(2)	-1589(3)	5578(2)	32(1)
C(128)	8196(2)	-2079(4)	5630(3)	36(1)
N(129)	8074(2)	-2691(3)	5222(2)	34(1)
C(130)	8463(3)	-3229(4)	5269(3)	44(2)
C(131)	8969(3)	-3154(5)	5701(3)	54(2)
C(132)	9090(3)	-2504(5)	6103(3)	54(2)
C(133)	8690(3)	-1970(4)	6076(3)	43(2)
C(134)	7349(2)	-2066(4)	5662(3)	35(1)
N(135)	7141(2)	-2692(3)	5274(2)	33(1)
C(136)	6810(3)	-3237(4)	5362(3)	43(2)
C(137)	6676(3)	-3131(4)	5814(3)	48(2)
C(138)	6883(3)	-2466(4)	6196(3)	49(2)
C(139)	7240(3)	-1924(4)	6127(3)	43(2)
N(140)	6742(2)	2072(3)	6091(2)	25(1)
C(141)	6351(2)	1610(3)	6189(3)	28(1)
N(142)	5871(2)	1940(3)	5927(2)	28(1)
C(143)	5488(2)	1588(4)	6034(3)	37(1)
C(144)	5573(3)	894(4)	6391(3)	42(2)
C(145)	6079(3)	558(4)	6661(3)	37(1)
C(146)	6476(2)	922(4)	6556(3)	32(1)

C(147)	6836(2)	2915(3)	6326(2)	28(1)
N(148)	6421(2)	3425(3)	6076(2)	28(1)
C(149)	6458(3)	4209(4)	6299(3)	39(2)
C(150)	6909(3)	4489(4)	6754(3)	48(2)
C(151)	7341(3)	3961(4)	6996(3)	47(2)
C(152)	7307(2)	3148(4)	6788(3)	35(1)
Cl(4)	8286(1)	-390(2)	2175(1)	72(1)
O(401)	8687(2)	-869(5)	2089(3)	85(2)
O(402)	8195(3)	392(4)	1862(3)	84(2)
O(403)	8446(2)	-205(4)	2789(2)	77(2)
O(404)	7817(2)	-889(5)	1964(2)	86(2)
Cl(5)	10000	-1312(2)	7500	55(1)
O(501)	9719(3)	-870(5)	6989(4)	112(3)
O(502)	9672(4)	-1895(7)	7619(4)	130(3)
Cl(6)	5001(3)	366(2)	2428(3)	34(1)
O(601)	4776(3)	67(4)	1838(3)	39(2)
O(602)	4800(3)	1189(4)	2446(4)	46(3)
O(603)	5560(3)	416(5)	2643(4)	66(3)
O(604)	4869(4)	-198(5)	2786(4)	51(3)
Cl(7)	6939(1)	1298(2)	2686(1)	73(1)
O(701)	6514(2)	1633(5)	2190(3)	94(2)
O(702)	7228(3)	1932(5)	3097(3)	105(3)
O(703)	6731(3)	712(6)	2957(3)	114(3)
O(704)	7285(5)	946(11)	2519(7)	237(7)
C(800)	5953(4)	-332(5)	4766(4)	70(2)
Cl(81)	5541(1)	84(1)	4994(1)	71(1)
Cl(82)	6005(1)	-1444(1)	4800(1)	63(1)
C(850)	8819(4)	-387(6)	4778(6)	90(3)
Cl(86)	9432(1)	26(1)	4987(1)	64(1)
Cl(87)	8783(1)	-1473(1)	4700(1)	57(1)
C(900)	7612(3)	4092(4)	5269(4)	50(2)
Cl(91)	8238(1)	4560(1)	5534(1)	71(1)
Cl(92)	7220(1)	4530(1)	5574(1)	58(1)

Table S5. Bond lengths [Å] and angles [°] for complex **5**.

Cu(1)-N(16)	2.012(6)	C(37)-C(38)	1.397(10)
Cu(1)-N(116)	2.025(5)	C(38)-C(39)	1.381(9)
Cu(1)-N(22)	2.026(5)	N(40)-C(47)	1.434(6)
Cu(1)-N(122)	2.037(6)	N(40)-C(41)	1.438(7)
Cu(1)-Cl(1)	2.3989(16)	C(41)-N(42)	1.336(7)
Cu(2)-N(135)	2.010(5)	C(41)-C(46)	1.382(8)
Cu(2)-N(29)	2.010(5)	N(42)-C(43)	1.348(7)
Cu(2)-N(129)	2.012(5)	C(43)-C(44)	1.350(9)
Cu(2)-N(35)	2.030(5)	C(44)-C(45)	1.373(9)
Cu(2)-Cl(2)	2.3944(16)	C(45)-C(46)	1.397(8)
Cu(3)-N(42)	2.004(5)	C(47)-N(48)	1.329(7)
Cu(3)-N(148)	2.021(5)	C(47)-C(52)	1.388(8)
Cu(3)-N(48)	2.030(5)	N(48)-C(49)	1.349(7)
Cu(3)-N(142)	2.035(5)	C(49)-C(50)	1.367(8)
Cu(3)-Cl(3)	2.3859(15)	C(50)-C(51)	1.390(8)
N(1)-C(2)	1.323(7)	C(51)-C(52)	1.369(8)
N(1)-C(12)	1.335(6)	N(101)-C(102)	1.306(7)
C(2)-N(3)	1.323(7)	N(101)-C(112)	1.358(7)
C(2)-N(13)	1.407(6)	C(102)-N(103)	1.333(7)
N(3)-C(4)	1.333(7)	C(102)-N(113)	1.394(7)
C(4)-N(5)	1.348(7)	N(103)-C(104)	1.335(7)
C(4)-N(14)	1.370(7)	C(104)-N(105)	1.338(7)
N(5)-C(6)	1.331(7)	C(104)-N(114)	1.379(7)
C(6)-N(7)	1.324(7)	N(105)-C(106)	1.315(7)
C(6)-N(13)	1.386(7)	C(106)-N(107)	1.327(7)
N(7)-C(8)	1.341(7)	C(106)-N(113)	1.408(7)
C(8)-N(9)	1.330(7)	N(107)-C(108)	1.337(7)
C(8)-N(27)	1.369(7)	C(108)-N(109)	1.336(7)
N(9)-C(10)	1.327(7)	C(108)-N(127)	1.380(7)
C(10)-N(11)	1.331(6)	N(109)-C(110)	1.333(7)
C(10)-N(13)	1.395(6)	C(110)-N(111)	1.315(7)
N(11)-C(12)	1.342(6)	C(110)-N(113)	1.394(7)
C(12)-N(40)	1.365(7)	N(111)-C(112)	1.319(7)
N(14)-C(15)	1.446(7)	C(112)-N(140)	1.370(7)
N(14)-C(21)	1.451(7)	N(114)-C(115)	1.436(7)
C(15)-N(16)	1.342(8)	N(114)-C(121)	1.444(8)
C(15)-C(20)	1.372(10)	C(115)-N(116)	1.329(8)
N(16)-C(17)	1.348(8)	C(115)-C(120)	1.370(9)
C(17)-C(18)	1.369(10)	N(116)-C(117)	1.355(8)
C(18)-C(19)	1.391(10)	C(117)-C(118)	1.352(10)
C(19)-C(20)	1.381(9)	C(118)-C(119)	1.384(10)
C(21)-N(22)	1.344(8)	C(119)-C(120)	1.403(9)
C(21)-C(26)	1.363(9)	C(121)-N(122)	1.315(9)
N(22)-C(23)	1.348(7)	C(121)-C(126)	1.373(10)
C(23)-C(24)	1.365(9)	N(122)-C(123)	1.361(8)
C(24)-C(25)	1.390(9)	C(123)-C(124)	1.358(11)
C(25)-C(26)	1.379(8)	C(124)-C(125)	1.357(12)
N(27)-C(28)	1.418(7)	C(125)-C(126)	1.394(10)
N(27)-C(34)	1.443(7)	N(127)-C(134)	1.442(8)
C(28)-N(29)	1.340(7)	N(127)-C(128)	1.443(7)
C(28)-C(33)	1.396(9)	C(128)-N(129)	1.349(8)
N(29)-C(30)	1.349(7)	C(128)-C(133)	1.374(9)
C(30)-C(31)	1.368(10)	N(129)-C(130)	1.353(8)
C(31)-C(32)	1.401(10)	C(130)-C(131)	1.379(10)
C(32)-C(33)	1.362(9)	C(131)-C(132)	1.384(10)
C(34)-N(35)	1.331(7)	C(132)-C(133)	1.389(9)
C(34)-C(39)	1.381(8)	C(134)-N(135)	1.342(8)
N(35)-C(36)	1.339(7)	C(134)-C(139)	1.361(9)
		N(135)-C(136)	1.361(8)
		C(136)-C(137)	1.363(10)
C(36)-C(37)	1.355(10)	C(137)-C(138)	1.380(10)

C(138)-C(139)	1.392(10)
N(140)-C(141)	1.435(7)
N(140)-C(147)	1.441(7)
C(141)-N(142)	1.330(7)
C(141)-C(146)	1.378(8)
N(142)-C(143)	1.346(7)
C(143)-C(144)	1.379(9)
C(144)-C(145)	1.394(9)
C(145)-C(146)	1.385(8)
C(147)-N(148)	1.335(7)
C(147)-C(152)	1.389(8)
N(148)-C(149)	1.352(7)
C(149)-C(150)	1.370(9)
C(150)-C(151)	1.385(10)
C(151)-C(152)	1.381(9)
Cl(4)-O(404)	1.434(6)
Cl(4)-O(402)	1.435(6)
Cl(4)-O(403)	1.453(6)
Cl(4)-O(401)	1.455(7)
Cl(5)-O(501)	1.383(7)
Cl(5)-O(501)#1	1.383(7)
Cl(5)-O(502)#1	1.431(8)
Cl(5)-O(502)	1.431(8)
Cl(6)-Cl(6)#2	0.365(12)
Cl(6)-O(604)#2	1.184(9)
Cl(6)-O(602)#2	1.403(6)
Cl(6)-O(601)	1.431(5)
Cl(6)-O(603)	1.432(5)
Cl(6)-O(604)	1.432(5)
Cl(6)-O(602)	1.432(5)
Cl(6)-O(603)#2	1.514(13)
Cl(6)-O(601)#2	1.753(11)
O(601)-O(604)#2	1.125(12)
O(601)-Cl(6)#2	1.753(11)
O(602)-O(602)#2	1.040(16)
O(602)-Cl(6)#2	1.403(6)
O(602)-O(603)#2	1.545(13)
O(603)-Cl(6)#2	1.514(13)
O(603)-O(602)#2	1.545(13)
O(603)-O(604)#2	1.569(13)
O(604)-O(601)#2	1.125(12)
O(604)-Cl(6)#2	1.184(9)
O(604)-O(603)#2	1.568(13)
Cl(7)-O(704)	1.342(10)
Cl(7)-O(701)	1.412(6)
Cl(7)-O(702)	1.424(8)
Cl(7)-O(703)	1.425(8)
C(800)-Cl(81)	1.644(10)
C(800)-Cl(82)	1.769(8)
C(850)-Cl(86)	1.706(10)
C(850)-Cl(87)	1.732(10)
C(900)-Cl(92)	1.746(7)
C(900)-Cl(91)	1.760(7)

N(16)-Cu(1)-N(116)	92.0(2)
N(16)-Cu(1)-N(22)	84.9(2)
N(116)-Cu(1)-N(22)	161.0(2)
N(16)-Cu(1)-N(122)	159.0(2)
N(116)-Cu(1)-N(122)	84.1(2)
N(22)-Cu(1)-N(122)	92.0(2)
N(16)-Cu(1)-Cl(1)	98.92(15)
N(116)-Cu(1)-Cl(1)	99.85(15)
N(22)-Cu(1)-Cl(1)	99.17(14)
N(122)-Cu(1)-Cl(1)	102.05(15)
N(135)-Cu(2)-N(29)	159.95(19)
N(135)-Cu(2)-N(129)	84.0(2)
N(29)-Cu(2)-N(129)	92.5(2)
N(135)-Cu(2)-N(35)	91.7(2)
N(29)-Cu(2)-N(35)	84.8(2)
N(129)-Cu(2)-N(35)	159.75(19)
N(135)-Cu(2)-Cl(2)	102.53(14)
N(29)-Cu(2)-Cl(2)	97.50(14)
N(129)-Cu(2)-Cl(2)	102.46(14)
N(35)-Cu(2)-Cl(2)	97.79(14)
N(42)-Cu(3)-N(148)	159.99(18)
N(42)-Cu(3)-N(48)	84.61(19)
N(148)-Cu(3)-N(48)	91.35(19)
N(42)-Cu(3)-N(142)	91.73(19)
N(148)-Cu(3)-N(142)	85.59(19)
N(48)-Cu(3)-N(142)	160.60(18)
N(42)-Cu(3)-Cl(3)	98.80(14)
N(148)-Cu(3)-Cl(3)	101.22(14)
N(48)-Cu(3)-Cl(3)	100.63(13)
N(142)-Cu(3)-Cl(3)	98.75(13)
C(2)-N(1)-C(12)	116.8(4)
N(1)-C(2)-N(3)	121.1(5)
N(1)-C(2)-N(13)	119.5(4)
N(3)-C(2)-N(13)	119.4(4)
C(2)-N(3)-C(4)	116.3(4)
N(3)-C(4)-N(5)	128.3(5)
N(3)-C(4)-N(14)	116.8(5)
N(5)-C(4)-N(14)	114.8(5)
C(6)-N(5)-C(4)	115.3(5)
N(7)-C(6)-N(5)	119.8(5)
N(7)-C(6)-N(13)	120.1(5)
N(5)-C(6)-N(13)	120.1(5)
C(6)-N(7)-C(8)	115.4(5)
N(9)-C(8)-N(7)	128.5(5)
N(9)-C(8)-N(27)	116.0(5)
N(7)-C(8)-N(27)	115.5(5)
C(10)-N(9)-C(8)	116.0(4)
N(9)-C(10)-N(11)	120.3(5)
N(9)-C(10)-N(13)	119.3(4)
N(11)-C(10)-N(13)	120.3(4)
C(10)-N(11)-C(12)	115.7(4)
N(1)-C(12)-N(11)	128.0(5)
N(1)-C(12)-N(40)	116.9(4)
N(11)-C(12)-N(40)	115.1(4)
C(6)-N(13)-C(10)	120.3(4)
C(6)-N(13)-C(2)	120.1(4)
C(10)-N(13)-C(2)	119.6(4)
C(4)-N(14)-C(15)	121.9(4)
C(4)-N(14)-C(21)	121.8(4)
C(15)-N(14)-C(21)	113.2(4)
N(16)-C(15)-C(20)	123.5(5)
N(16)-C(15)-N(14)	114.0(5)
C(20)-C(15)-N(14)	122.2(5)
C(15)-N(16)-C(17)	117.8(6)
C(15)-N(16)-Cu(1)	119.1(4)
C(17)-N(16)-Cu(1)	122.9(4)

N(16)-C(17)-C(18)	122.2(6)	C(102)-N(101)-C(112)	114.7(5)
C(17)-C(18)-C(19)	119.4(6)	N(101)-C(102)-N(103)	119.6(5)
C(20)-C(19)-C(18)	118.8(7)	N(101)-C(102)-N(113)	120.2(5)
C(15)-C(20)-C(19)	118.3(6)	N(103)-C(102)-N(113)	120.2(5)
N(22)-C(21)-C(26)	123.9(5)	C(102)-N(103)-C(104)	115.0(5)
N(22)-C(21)-N(14)	113.4(5)	N(103)-C(104)-N(105)	129.0(5)
C(26)-C(21)-N(14)	122.4(5)	N(103)-C(104)-N(114)	114.8(5)
C(21)-N(22)-C(23)	117.4(5)	N(105)-C(104)-N(114)	116.2(5)
C(21)-N(22)-Cu(1)	119.1(4)	C(106)-N(105)-C(104)	116.2(5)
C(23)-N(22)-Cu(1)	123.3(4)	N(105)-C(106)-N(107)	120.9(5)
N(22)-C(23)-C(24)	122.3(6)	N(105)-C(106)-N(113)	119.5(5)
C(23)-C(24)-C(25)	119.2(6)	N(107)-C(106)-N(113)	119.6(5)
C(26)-C(25)-C(24)	119.2(6)	C(106)-N(107)-C(108)	115.4(5)
C(21)-C(26)-C(25)	118.0(6)	N(109)-C(108)-N(107)	128.8(5)
C(8)-N(27)-C(28)	122.1(5)	N(109)-C(108)-N(127)	115.6(5)
C(8)-N(27)-C(34)	121.7(4)	N(107)-C(108)-N(127)	115.5(5)
C(28)-N(27)-C(34)	115.2(4)	C(110)-N(109)-C(108)	115.8(5)
N(29)-C(28)-C(33)	121.9(5)	N(111)-C(110)-N(109)	120.9(5)
N(29)-C(28)-N(27)	115.8(5)	N(111)-C(110)-N(113)	119.9(5)
C(33)-C(28)-N(27)	122.0(5)	N(109)-C(110)-N(113)	119.2(5)
C(28)-N(29)-C(30)	118.7(5)	C(110)-N(111)-C(112)	115.3(5)
C(28)-N(29)-Cu(2)	118.7(4)	N(111)-C(112)-N(101)	128.6(5)
C(30)-N(29)-Cu(2)	122.6(4)	N(111)-C(112)-N(140)	117.0(5)
N(29)-C(30)-C(31)	122.7(6)	N(101)-C(112)-N(140)	114.3(5)
C(30)-C(31)-C(32)	118.0(6)	C(102)-N(113)-C(110)	119.8(4)
C(33)-C(32)-C(31)	120.1(6)	C(102)-N(113)-C(106)	119.8(4)
C(32)-C(33)-C(28)	118.5(6)	C(110)-N(113)-C(106)	120.4(4)
N(35)-C(34)-C(39)	122.9(5)	C(104)-N(114)-C(115)	121.1(5)
N(35)-C(34)-N(27)	115.0(5)	C(104)-N(114)-C(121)	122.5(5)
C(39)-C(34)-N(27)	122.1(5)	C(115)-N(114)-C(121)	114.6(5)
C(34)-N(35)-C(36)	118.5(5)	N(116)-C(115)-C(120)	124.3(5)
C(34)-N(35)-Cu(2)	119.1(4)	N(116)-C(115)-N(114)	113.6(5)
C(36)-N(35)-Cu(2)	122.3(4)	C(120)-C(115)-N(114)	121.9(6)
N(35)-C(36)-C(37)	122.7(6)	C(115)-N(116)-C(117)	117.7(6)
C(36)-C(37)-C(38)	118.8(6)	C(115)-N(116)-Cu(1)	118.0(4)
C(39)-C(38)-C(37)	119.1(6)	C(117)-N(116)-Cu(1)	124.2(5)
C(34)-C(39)-C(38)	118.0(6)	C(118)-C(117)-N(116)	122.1(7)
C(12)-N(40)-C(47)	121.7(4)	C(117)-C(118)-C(119)	120.1(6)
C(12)-N(40)-C(41)	122.5(4)	C(118)-C(119)-C(120)	118.6(7)
C(47)-N(40)-C(41)	113.3(4)	C(115)-C(120)-C(119)	117.3(6)
N(42)-C(41)-C(46)	123.0(5)	N(122)-C(121)-C(126)	123.8(6)
N(42)-C(41)-N(40)	114.9(5)	N(122)-C(121)-N(114)	114.0(6)
C(46)-C(41)-N(40)	121.8(5)	C(126)-C(121)-N(114)	121.8(7)
C(41)-N(42)-C(43)	117.7(5)	C(121)-N(122)-C(123)	118.2(7)
C(41)-N(42)-Cu(3)	118.7(4)	C(121)-N(122)-Cu(1)	117.6(4)
C(43)-N(42)-Cu(3)	123.4(4)	C(123)-N(122)-Cu(1)	124.2(6)
N(42)-C(43)-C(44)	122.9(6)	C(124)-C(123)-N(122)	121.9(8)
C(43)-C(44)-C(45)	119.7(5)	C(125)-C(124)-C(123)	119.0(7)
C(44)-C(45)-C(46)	118.8(6)	C(124)-C(125)-C(126)	120.5(8)
C(41)-C(46)-C(45)	117.8(5)	C(121)-C(126)-C(125)	116.7(8)
N(48)-C(47)-C(52)	123.4(5)	C(108)-N(127)-C(134)	121.3(5)
N(48)-C(47)-N(40)	114.9(5)	C(108)-N(127)-C(128)	122.0(5)
C(52)-C(47)-N(40)	121.3(5)	C(134)-N(127)-C(128)	114.3(5)
C(47)-N(48)-C(49)	117.8(5)	N(129)-C(128)-C(133)	123.6(6)
C(47)-N(48)-Cu(3)	118.3(4)	N(129)-C(128)-N(127)	113.2(5)
C(49)-N(48)-Cu(3)	123.8(4)	C(133)-C(128)-N(127)	123.0(6)
N(48)-C(49)-C(50)	122.5(5)	C(128)-N(129)-C(130)	117.3(5)
C(49)-C(50)-C(51)	118.9(5)	C(128)-N(129)-Cu(2)	117.9(4)
C(52)-C(51)-C(50)	119.4(6)	C(130)-N(129)-Cu(2)	124.9(4)
C(51)-C(52)-C(47)	118.0(5)	N(129)-C(130)-C(131)	122.5(6)

C(130)-C(131)-C(132)	119.2(6)
C(131)-C(132)-C(133)	118.9(7)
C(128)-C(133)-C(132)	118.4(6)
N(135)-C(134)-C(139)	124.5(6)
N(135)-C(134)-N(127)	113.6(5)
C(139)-C(134)-N(127)	121.6(6)
C(134)-N(135)-C(136)	117.6(6)
C(134)-N(135)-Cu(2)	117.6(4)
C(136)-N(135)-Cu(2)	124.8(4)
N(135)-C(136)-C(137)	121.3(6)
C(136)-C(137)-C(138)	119.9(7)
C(137)-C(138)-C(139)	119.5(7)
C(134)-C(139)-C(138)	117.1(7)
C(112)-N(140)-C(141)	121.2(4)
C(112)-N(140)-C(147)	122.0(4)
C(141)-N(140)-C(147)	114.9(4)
N(142)-C(141)-C(146)	124.0(5)
N(142)-C(141)-N(140)	113.9(5)
C(146)-C(141)-N(140)	122.0(5)
C(141)-N(142)-C(143)	117.9(5)
C(141)-N(142)-Cu(3)	116.8(4)
C(143)-N(142)-Cu(3)	125.4(4)
N(142)-C(143)-C(144)	122.5(6)
C(143)-C(144)-C(145)	118.6(6)
C(146)-C(145)-C(144)	119.1(6)
C(141)-C(146)-C(145)	117.9(6)
N(148)-C(147)-C(152)	124.1(5)
N(148)-C(147)-N(140)	113.6(5)
C(152)-C(147)-N(140)	122.2(5)
C(147)-N(148)-C(149)	117.8(5)
C(147)-N(148)-Cu(3)	117.1(4)
C(149)-N(148)-Cu(3)	125.1(4)
N(148)-C(149)-C(150)	121.8(6)
C(149)-C(150)-C(151)	119.7(6)
C(152)-C(151)-C(150)	119.6(6)
C(151)-C(152)-C(147)	117.0(6)
O(404)-Cl(4)-O(402)	110.8(4)
O(404)-Cl(4)-O(403)	108.6(4)
O(402)-Cl(4)-O(403)	108.4(4)
O(404)-Cl(4)-O(401)	108.0(5)
O(402)-Cl(4)-O(401)	109.5(4)
O(403)-Cl(4)-O(401)	111.5(4)
O(501)-Cl(5)-O(501)#1	119.1(7)
O(501)-Cl(5)-O(502)#1	106.9(6)
O(501)#1-Cl(5)-O(502)#1	111.4(5)
O(501)-Cl(5)-O(502)	111.4(5)
O(501)#1-Cl(5)-O(502)	106.9(6)
O(502)#1-Cl(5)-O(502)	99.4(9)
O(601)-Cl(6)-O(603)	109.5(4)
O(601)-Cl(6)-O(604)	109.7(4)
O(603)-Cl(6)-O(604)	109.8(4)
O(601)-Cl(6)-O(602)	109.4(4)
O(603)-Cl(6)-O(602)	108.8(4)
O(604)-Cl(6)-O(602)	109.7(4)
O(704)-Cl(7)-O(701)	109.2(8)
O(704)-Cl(7)-O(702)	105.1(8)
O(701)-Cl(7)-O(702)	112.5(5)
O(704)-Cl(7)-O(703)	112.8(9)
O(701)-Cl(7)-O(703)	107.9(5)
O(702)-Cl(7)-O(703)	109.4(5)
Cl(81)-C(800)-Cl(82)	116.1(5)
Cl(86)-C(850)-Cl(87)	114.8(5)
Cl(92)-C(900)-Cl(91)	112.7(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+3/2 #2 -x+1,y,-z+1/2

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