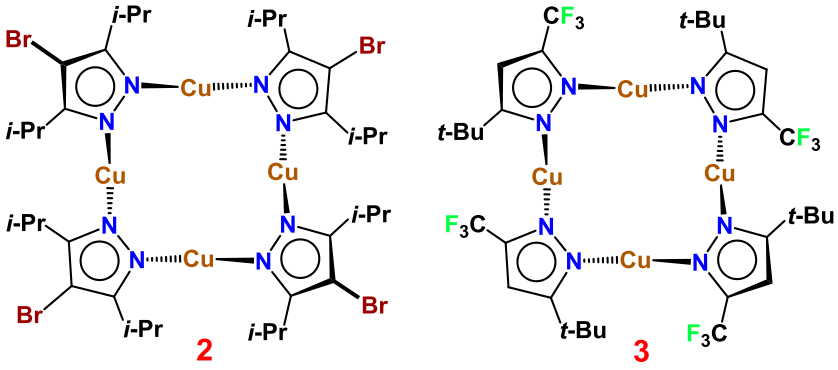
Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Brightly Phosphorescent Tetranuclear Copper(I) Pyrazolates

H. V. Rasika Dias, *[a] Himashinie V. K. Diyabalanage, [a] Mukunda M. Ghimire, [b] Joshua M. Hudson, [c] Devaborniny Parasar, [a] Chammi S. Palehepitiya Gamage, [a] Shan Li, [c] and Mohammad A. Omary*[c]

E-mail address of corresponding authors: dias@uta.edu; omary@unt.edu



a. *Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, USA.*

b. *Department of Chemistry, Lebanon Valley College, 101 College Ave, Annville, PA, 17003, USA.*

c. *Department of Chemistry, University of North Texas, 1508 W Mulberry St, Denton, TX, 76201, USA.*

Materials and Experimental Methods

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmosphere single-station drybox equipped with a -25 °C refrigerator. Solvents were purchased from commercial sources, distilled from conventional drying agents, and degassed by the freeze-pump-thaw method twice prior to use. The glassware was oven-dried at 150 °C overnight. NMR spectra were recorded at 25 °C on a JEOL Eclipse 500 and JEOL Eclipse 300 spectrometer (^{1}H, 500.16 MHz and 300.53 MHz; ^{13}C, 125.78 MHz, and 75.57 MHz; ^{19}F, 470.62 MHz, and 282.78 MHz), unless otherwise noted. Proton and carbon chemical shifts are reported in parts per million versus Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$. Infrared spectra were recorded on a JASCO FT-IR 410 spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. [3,5-(*i*-Pr)$_2$,4-(Br)Pz]H and [3-(CF$_3$),5-(Bu^t)Pz]H were prepared using published methods.[1, 2]

Synthesis of {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ (2)

$[Cu(CH_3CN)_4]BF_4$ (0.25 g, 0.80 mmol) was dissolved in dry acetone (15.0 mL) under nitrogen in a Schlenk tube. To this, [3,5-(*i*-Pr)$_2$,4-(Br)Pz]H[1] (0.20 g, 0.87 mmol) in dry acetone (5.0 mL) was added while stirring. Then, dry triethylamine (0.3 mL) was added to the clear mixture over a period of 1 min. The product precipitated as a while solid. The resulting mixture was stirred for 4 h. The product was recovered by vacuum filtration, and then washed with acetone (5 mL) and hexane (5 mL). The X-ray quality crystals were obtained from hexane/toluene at -25 ºC. Yield: 85%. M.p.: 200-202 ºC. ^{1}H NMR ($CDCl_3$): δ 1.30 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, *i*-Pr-H), 1.35 (d, 6H, $^{3}J_{HH}$ = 6.9 Hz, *i*-Pr-H), 1.44 (d, 4.5H, $^{3}J_{HH}$ = 7.2 Hz, *i*-Pr-H), 3.07 (sept, 2H, $^{3}J_{HH}$ = 6.9 Hz, CH), 3.28 (sept,

0.6 H, $^{3}J_{HH}$ = 7.2 Hz, CH). These ^{1}H NMR peak ratios change at different concentrations indicating the presence of two species in equilibrium that interchange depending on the concentration. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 21.9 (s, *i*-Pr-C), 22.6 (s, *i*-Pr-C), 27.2 (s, *i*-Pr-C), 28.8 (s, *i*-Pr-C), 90.2 (s, C-4), 156.1 (s, C-3/C-5). Anal. Calc. for $C_{36}H_{56}N_8Br_4Cu_4$: C, 36.81; H, 4.81; N, 9.54. Found: C, 36.78; H,4.60; N, 9.51.

Synthesis of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ (3)

Cu_2O (0.4 g, 3.0 mmol) and [3-(CF_3),5-(Bu^t)Pz]H[2] (0.5 g, 2.6 mmol) were mixed in toluene (20.0 mL) and acetonitrile (3.0 mL). The mixture was refluxed for 12 h. After cooling, the solution was filtered through a bed of Celite to remove insoluble materials. The filtrate was collected and solvent was removed under reduced pressure to obtain {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ as a white solid. X-ray quality crystals were obtained from toluene at -25 ºC. Yield: 90%. M.p.: 246-248 ºC. ^{1}H NMR ($CDCl_3$): δ 1.33-1.40 (several singlets, 9H, Bu^t-H), 1.46 (s, 5H, Bu^t-H), 6.32-6.39 (several singlets, 1H, Pz-H), 6.46 (s, 0.5H, Pz-H); ^{19}F NMR (C_6D_6): δ -59.43 (br s, CF_3), -60.3 (s, CF_3), -60.3 to -61.0 (several additional small peaks, CF_3) ; $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 30.9 (Bu^t-C), 30.9 (Bu^t-C), 31.0-31.3 (several additional peaks for Bu^t-C), 31.5 (Bu^t-C), 31.6 (Bu^t-C), 101.5 (br s, C-4), 122.0 (q, $^{1}J_{CF}$ = 269.1 Hz, CF_3), 122.2 (q, $^{1}J_{CF}$ = 268.7 Hz, CF_3), 142.7 (br q, $^{2}J_{C\text{-}F}$ = 36.0 Hz, C-3), 142.9 (br q, $^{2}J_{C\text{-}F}$ = 36.8 Hz, C-3), 161.8 (C-5), 164.7 (C-5). Anal. Calc. for $C_{32}H_{40}N_8F_{12}Cu_4$: C, 37.72; H, 3.96; N, 11.00. Found: C, 37.70; H,3.90; N, 11.02.

X-ray Crystallographic Determination

A suitable crystal of the copper complex covered with a layer of hydrocarbon oil was selected and mounted with paratone-N oil in a cryo-loop, and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ and {[3-(CF_3),5-

(Bu^t)Pz]Cu}$_4$ were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with an Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å). The X-ray data of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ were also collected at 276(2) K using the same crystal to study the changes to Cu•••Cu separation upon warming. The detector was placed at a distance of 5.995 cm from the crystal. The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Crystals of {[3-(CF$_3$),5-(Bu^t)Pz]Cu}$_4$ were twinned, and the twin components were identified using the Cell_Now program. There were two major twin domains with unit cells related to each other by a rotation of 180° around the b-axis. Data were corrected for absorption effects using TWINABS. The CF$_3$ moieties and one of the *t*-Bu groups of {[3-(CF$_3$),5-(Bu^t)Pz]Cu}$_4$ show rotational disorder. These disorders were modeled successfully. All the non-hydrogen atoms were refined anisotropically. Two isopropyl groups of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ show positional disorder, which was also modeled satisfactorily. All the hydrogen atoms of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ and {[3-(CF$_3$),5-(Bu^t)Pz]Cu}$_4$ were placed at calculated positions and refined using a riding model. Structures were solved using Bruker SHELXTL software package, and refined by the least-squares method using SHELXL[3, 4]within Olex2[5] GUI. CCDC 1936960-1936962 files contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK). Figures S1 and S2 show the packing diagrams of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ and {[3-(CF$_3$),5-(Bu^t)Pz]Cu}$_4$, indicating that both species exist as discrete units with no significant intermolecular interactions. Further details are given in the CIF.

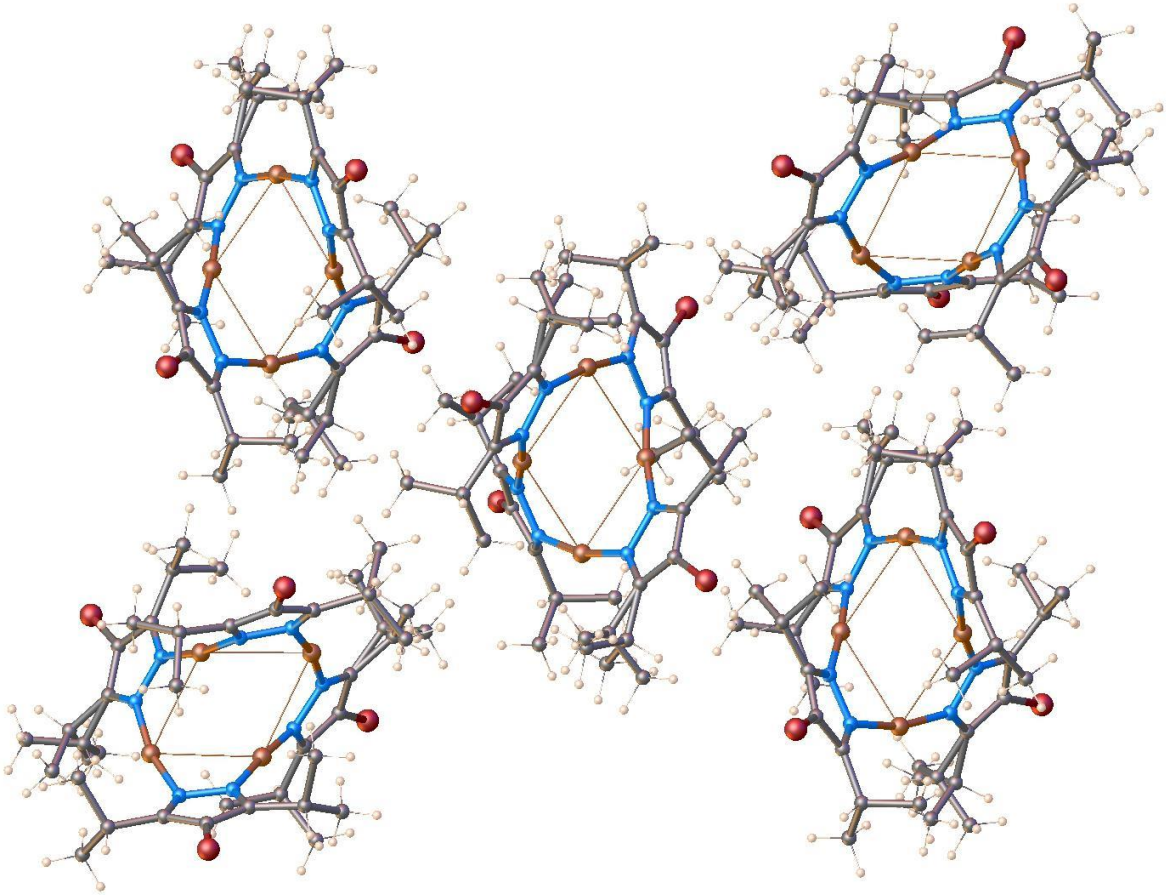


Figure S1. Packing diagram of $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ crystals.

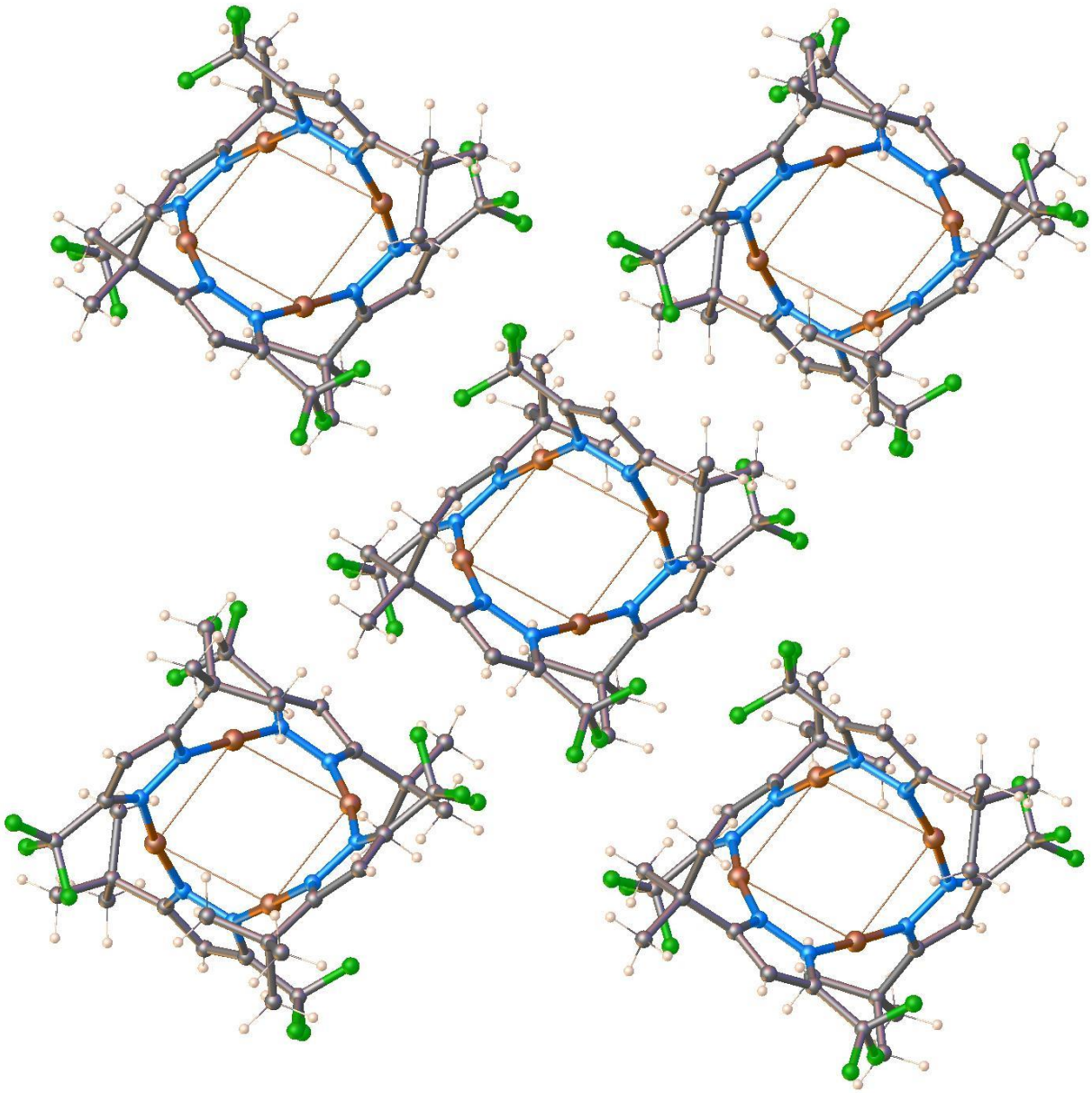


Figure S2. Packing diagram of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ crystals.

Photoluminescence Measurements

The luminescence measurements were carried out for sublimed crystalline powders. Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-4 scanning spectrofluorometer. The excitation and emission spectra were corrected for the wavelength-dependent lamp intensity and detector response, respectively. Lifetime data were acquired using fluorescence and phosphorescence sub-system add-ons to the PTI instrument. For the lifetimes of all complexes, the 337.1 nm line of the N_2 laser was used to pump a freshly prepared solutions of organic continuum laser dyes ($1x10^{-2}$ M) Coumarin-540A, or ($5x10^{-3}$ M) Rhodamine 590 in ethanol, the outputs of which were tuned and frequency doubled to attain the 275 or 290 nm excitations used to generate the lifetime and time dependent data. All samples were initially measured at 77 K using a Suprasil quartz cold finger Dewar filled with liquid nitrogen, and samples were held in Suprasil quartz sample tubes, all made here at the UNT Chemistry Department Glass shop. Temperature dependent measurements were carried out in an Oxford cryostat Optistat CF with liquid helium as the coolant, a non-emissive Cu based grease was used to ensure thermal conduction to the sample. Frozen solutions were made using dry degassed solvents, the solution was held in a 1mm path length cuvette and mounted in on the sample holder using Cu grease to hold it in place. The sample was placed in the light beam at a -45º angle to the detector and the emission was recorded from the back of the sample which minimized scattered light from the faces of the cuvette and sample. Absorption spectra were acquired with a Perkin-Elmer Lambda 900 double-beam UV/VIS/NIR spectrophotometer for solutions of crystalline samples prepared in freshly distilled and degassed THF using matching 1cm quartz cuvettes (Wilmad). Solid samples were measured by crushing the powder between two quartz slides with a 0.1 mm path (Wilmad) and using the Lab Sphere diffuse reflectance accessory to the Lambda 900, either in transmission or reflection modes. For transmission mode measurements a focusing lens was placed in front of the sample and the beam focused to a fine point illuminating an area with a small sample density.

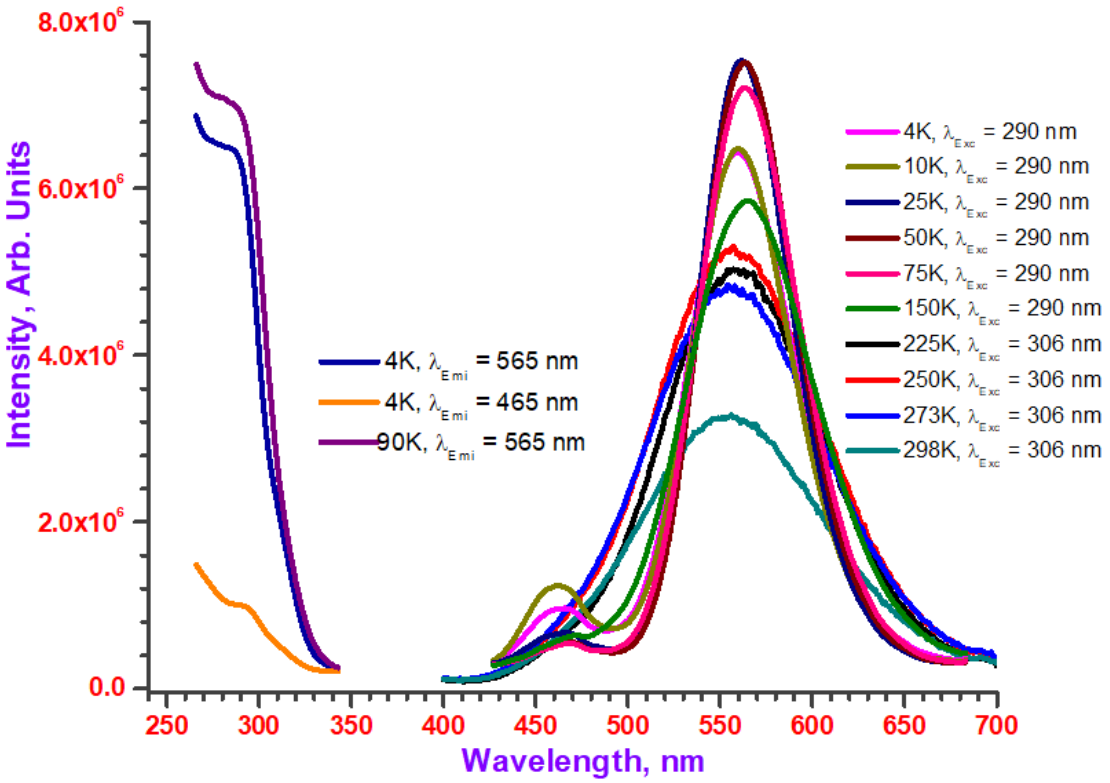


Figure S3. Solid-state excitation and emission spectra for $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ solid at various temperatures.

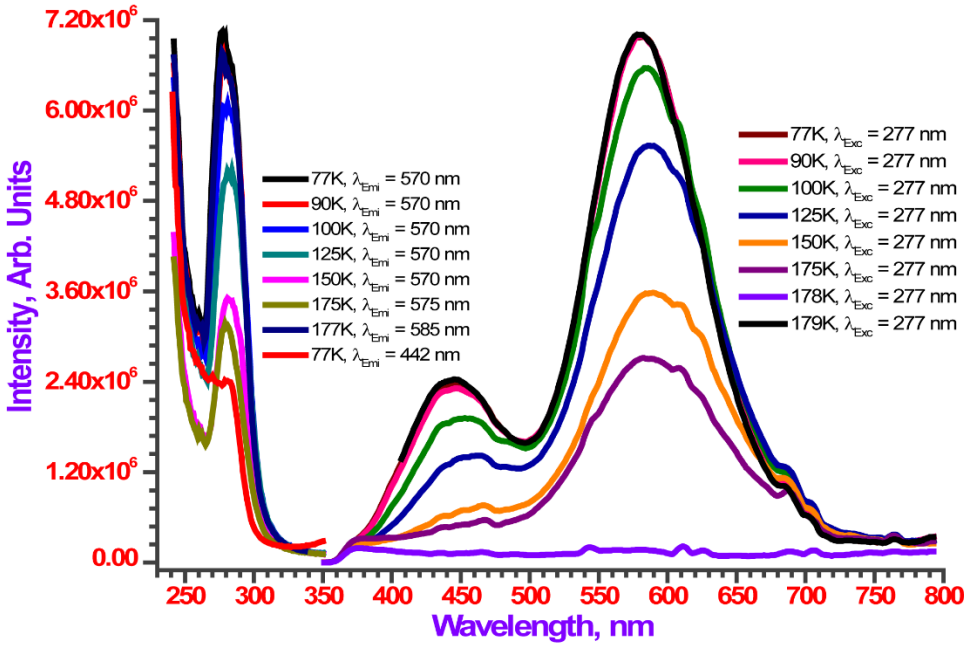


Figure S4. Emission spectrum for frozen solutions of $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ in toluene from 77 K to liquid solution, demonstrating the rigidochromism associated with these complexes.

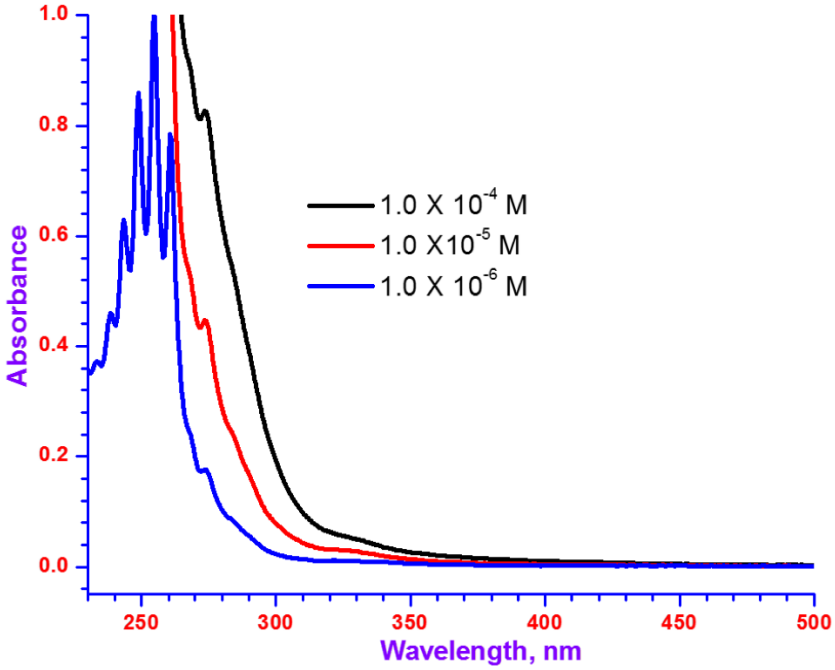


Figure S5. Electronic absorbance spectra of dilute THF solution of $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ at 298K.

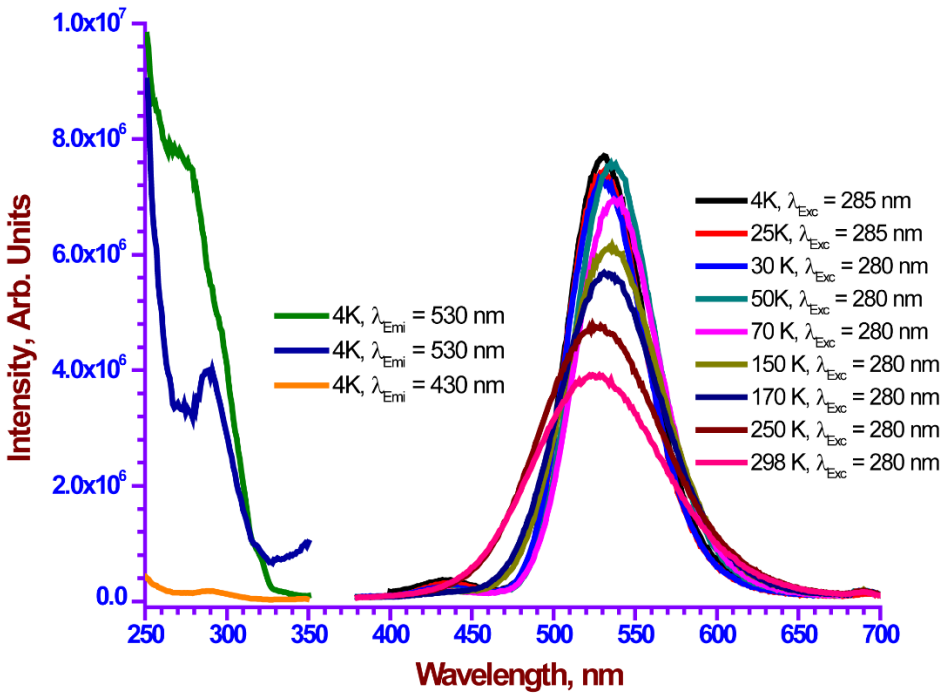


Figure S6. Solid-state excitation and emission spectra for {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ solid at various temperatures.

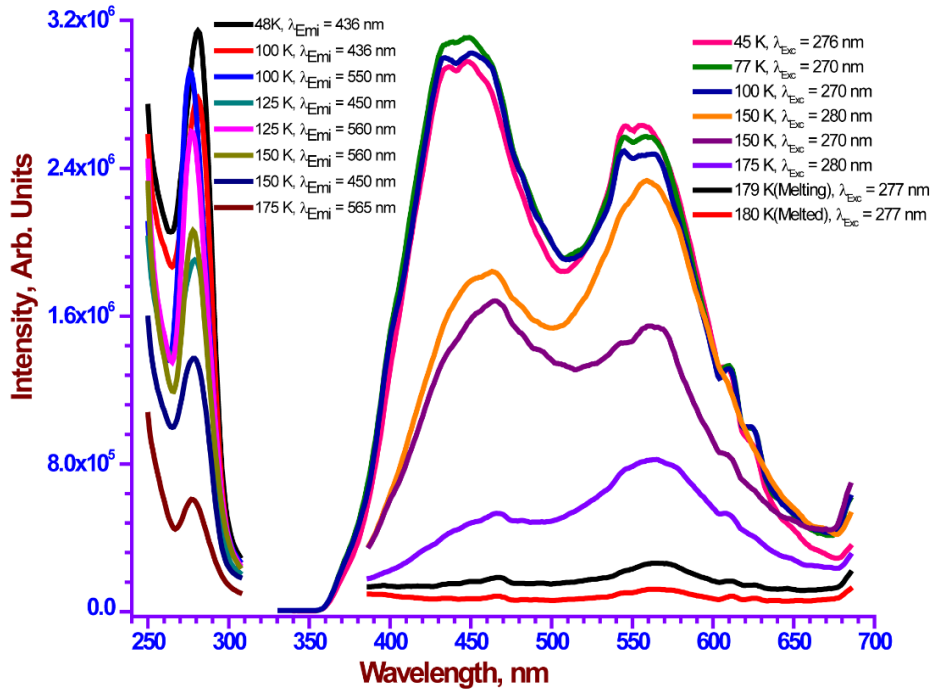


Figure S7. Emission spectrum for frozen solutions of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ in toluene from 77 K to liquid solution, demonstrating the rigidochromism associated with these complexes.

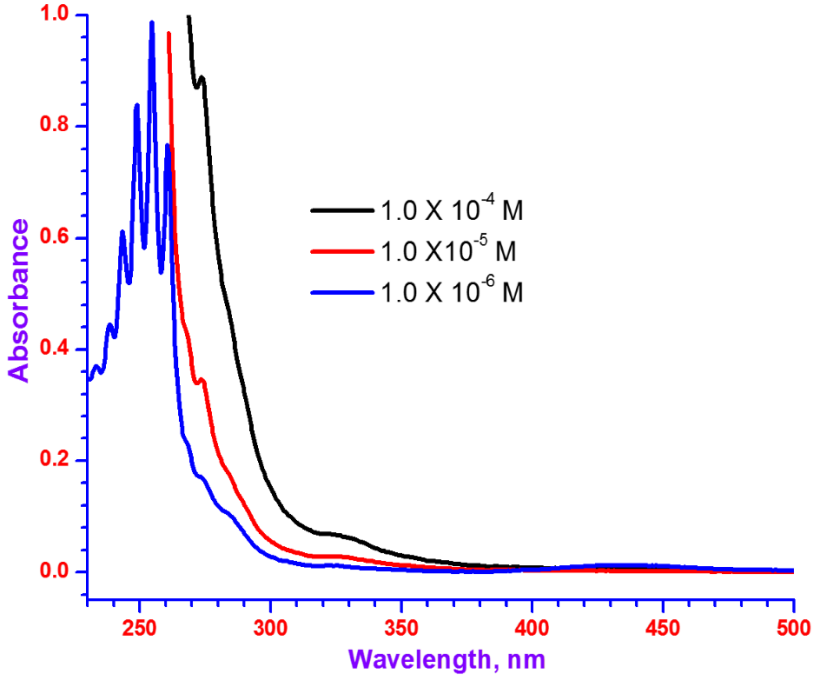


Figure S8. Electronic absorbance spectra of dilute THF solution of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ at 298K.

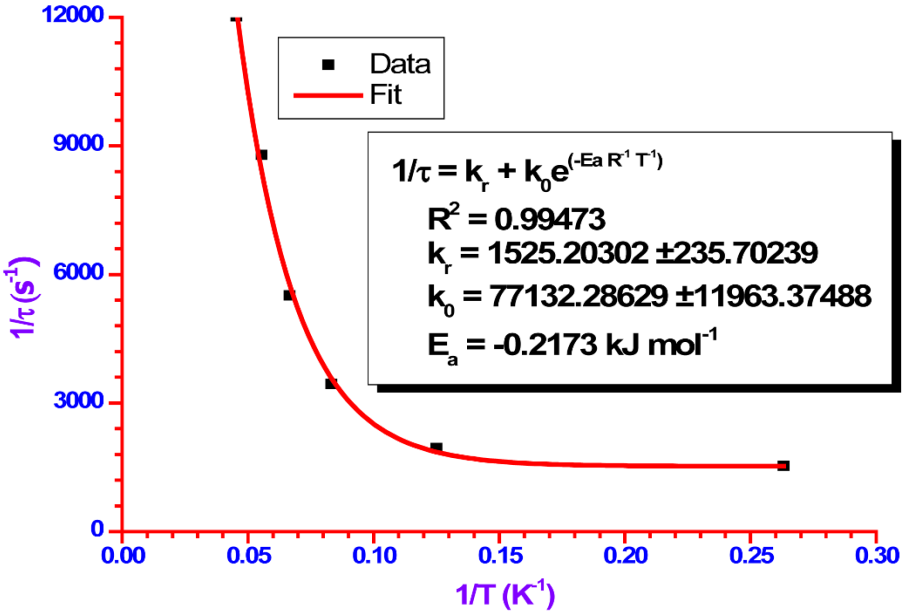


Figure S9. Fit of lifetime^{-1} *vs.* temperature^{-1} to give k_r and E_a for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$.

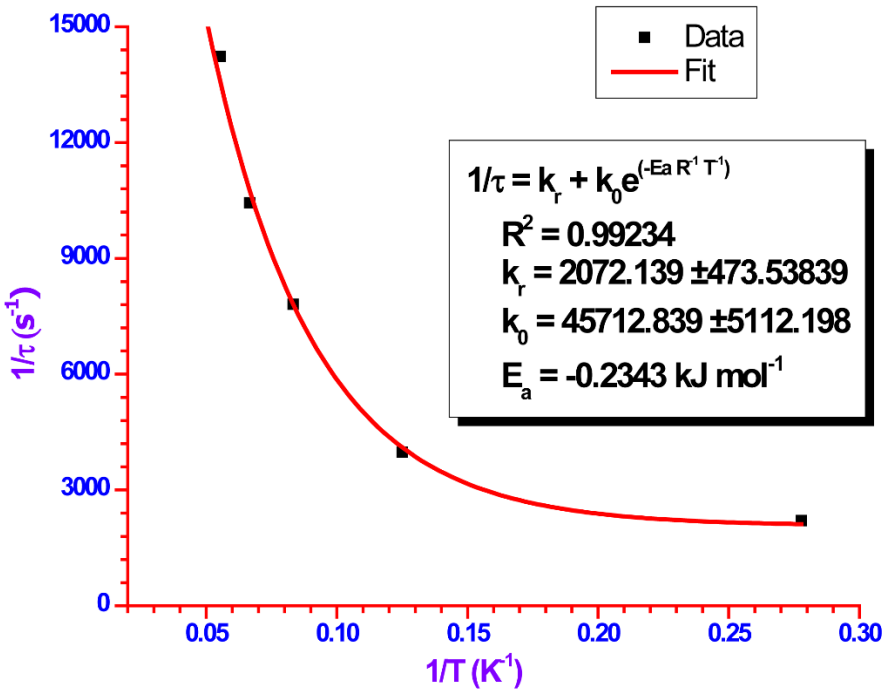


Figure S10. Fit of lifetime^{-1} *vs.* temperature^{-1} to give k_r, k_0, and E_a for {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$.

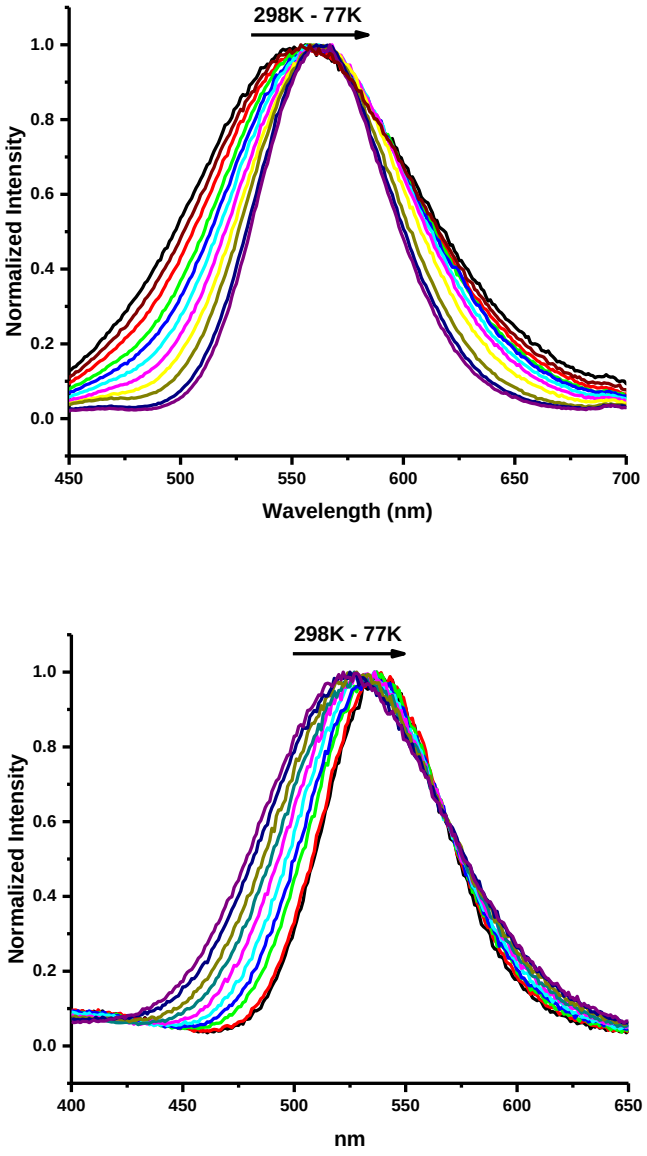
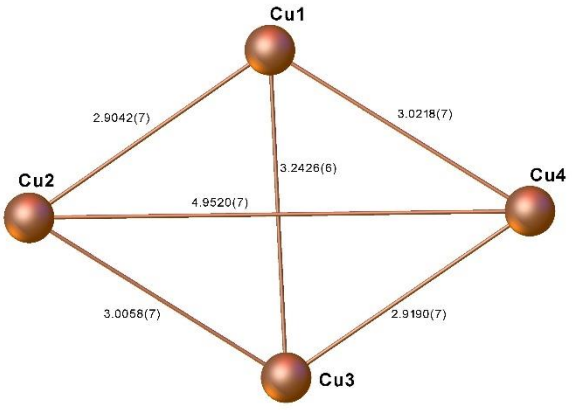


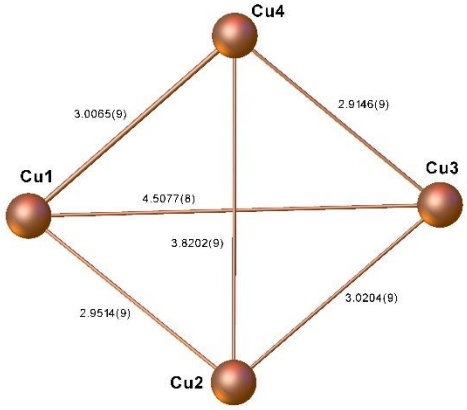
Figure S11. Normalized emission spectra for $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ solid (top) and $\{[3\text{-}(CF_3),5\text{-}(Bu^{t})Pz]Cu\}_4$ solid (bottom) at various temperatures, showing fine-tuning in the emission maxima.

Table S1. Comparative study of intra-molecular Cu•••Cu distances (Å) of tetranuclear copper(I) pyrazolates.

Complex	Cu•••Cu distance	Diagonal Cu•••Cu distance	Ref
{[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ at 100K	2.9042(7), 2.9190(7), 3.0058(7), 3.0218(7)	3.2426(6), 4.9520(7)	This work
{[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ at 276K	2.9361(8), 2.9509(8), 3.0029(8), 3.0231(8)	3.2677(8), 4.9733(9)	This work
{[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$	2.9146(9), 2.9514(9), 3.0065(9), 3.0204(9)	3.8202(9), 4.5077(8)	This work
{[3,5-(Ph)$_2$Pz]Cu}$_4$	3.088(2), 3.119(2), 3.131(2), 3.132(2)	4.366(2), 4.451(2)	[6]
{[3,5-(Bu^t)$_2$Pz]Cu}$_4$	2.963(1), 2.964(1), 2.972(1), 2.989(1)	3.393(1), 4.842(1)	[7, 8]
{[3-(Bu^t),5-(*i*-Pr)Pz]Cu}$_4$	3.071(2)	4.343(2)	[8, 9]
{[3,5-((Et)(Me)HCOC(O))$_2$Pz]Cu}$_4$	3.400(2), 3.403(2), 3.480(2), 3.532(2)	4.702(2), 5.061(2)	[7]
{[3-(ferrocenyl),5-(CF_3)Pz]Cu}$_4$	3.225(1)	4.538(1)	[10]



Cu$_4$ core of {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ at 100K



Cu$_4$ core of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ at 100K

Table S2. Crystal data and structure refinement for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ (100K)**.**

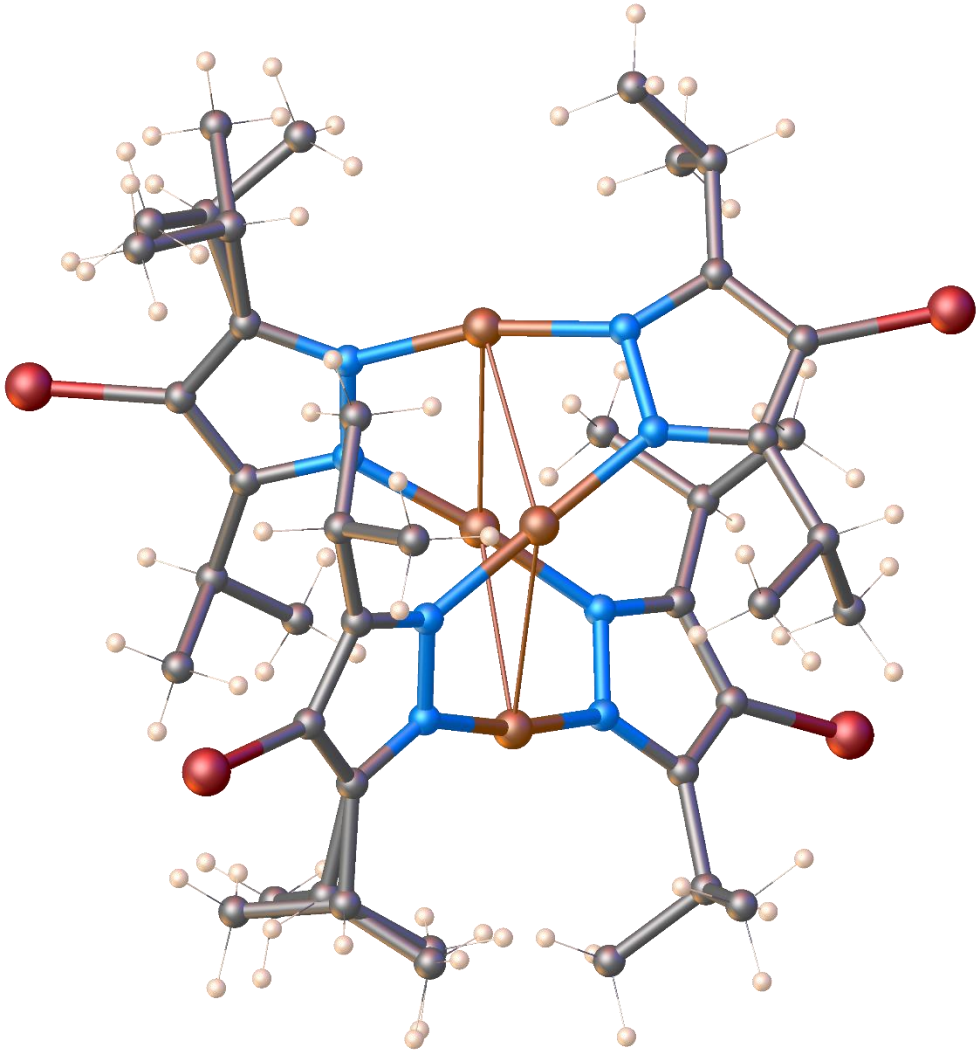


Figure S12. View showing the symmetric unit of {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ and iso-propyl group disorder.

Identification code	dias343s
Empirical formula	$C_{36}H_{56}Br_4Cu_4N_8$
Formula weight	1174.68
Temperature/K	100.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	18.9169(15)
b/Å	20.9151(16)
c/Å	22.8836(17)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	9053.9(12)
Z	8
ρ_{calc}g/cm^3	1.724
μ/mm^{-1}	5.419
F(000)	4672.0
Crystal size/mm^3	0.23 × 0.11 × 0.046
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.894 to 51.992
Index ranges	-23 ≤ h ≤ 23, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28
Reflections collected	68234
Independent reflections	8902 [R_{int} = 0.0655, R_{sigma} = 0.0397]
Data/restraints/parameters	8902/52/541
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0711
Final R indexes [all data]	R_1 = 0.0628, wR_2 = 0.0828
Largest diff. peak/hole / e Å^{-3}	1.02/-0.61

Table S3. Bond Lengths for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ (100K).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu2	2.9042(7)	C4	C6	1.526(6)
Cu1	Cu4	3.0218(7)	C7	C8	1.534(6)
Cu1	N1	1.858(3)	C7	C9	1.530(6)
Cu1	N8	1.852(3)	C10	C11	1.387(5)
Cu2	Cu3	3.0058(7)	C10	C13	1.498(6)
Cu2	N2	1.849(3)	C11	C12	1.383(5)
Cu2	N3	1.843(3)	C12	C16A	1.507(7)
Cu3	Cu4	2.9190(7)	C12	C16B	1.520(8)
Cu3	N4	1.864(3)	C13	C14	1.514(6)
Cu3	N5	1.870(3)	C13	C15	1.502(8)
Cu4	N6	1.861(3)	C16A	C17A	1.510(10)
Cu4	N7	1.857(3)	C16A	C18A	1.524(10)
N1	N2	1.390(4)	C16B	C17B	1.534(12)
N1	C3	1.337(5)	C16B	C18B	1.540(12)
N2	C1	1.348(5)	C19	C20	1.378(5)
N3	N4	1.386(4)	C19	C22	1.506(5)
N3	C12	1.346(5)	C20	C21	1.388(5)
N4	C10	1.344(5)	C21	C25	1.500(5)
N5	N6	1.394(4)	C22	C23	1.523(6)
N5	C21	1.346(5)	C22	C24	1.526(6)
N6	C19	1.343(5)	C25	C26	1.529(6)
N7	N8	1.391(4)	C25	C27	1.526(6)
N7	C30	1.348(5)	C28	C29	1.388(5)
N8	C28	1.345(5)	C28	C31	1.505(5)
Br1	C2	1.877(4)	C29	C30	1.387(5)
Br2	C11	1.874(4)	C30	C34	1.510(9)
Br3	C20	1.888(4)	C30	C34A	1.508(6)
Br4	C29	1.880(4)	C31	C32	1.523(6)
C1	C2	1.380(5)	C31	C33	1.531(6)
C1	C4	1.503(5)	C34	C35	1.528(8)
C2	C3	1.391(5)	C34	C36	1.528(8)
C3	C7	1.508(5)	C34A	C35A	1.529(6)
C4	C5	1.534(6)	C34A	C36A	1.525(6)

Table S4. Bond Angles for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ (100K).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu2	Cu1	Cu4	113.34(2)	C6	C4	C5	110.1(4)
N1	Cu1	Cu2	64.44(10)	C3	C7	C8	109.7(3)
N1	Cu1	Cu4	119.60(10)	C3	C7	C9	113.1(4)
N8	Cu1	Cu2	117.99(10)	C9	C7	C8	111.8(4)
N8	Cu1	Cu4	63.25(10)	N4	C10	C11	107.4(3)
N8	Cu1	N1	175.73(14)	N4	C10	C13	124.6(4)
Cu1	Cu2	Cu3	66.523(16)	C11	C10	C13	128.0(4)
N2	Cu2	Cu1	66.70(10)	C10	C11	Br2	125.4(3)
N2	Cu2	Cu3	101.07(10)	C12	C11	Br2	126.4(3)
N3	Cu2	Cu1	102.36(10)	C12	C11	C10	108.2(3)
N3	Cu2	Cu3	65.96(9)	N3	C12	C11	107.2(3)
N3	Cu2	N2	166.21(14)	N3	C12	C16A	128.0(5)
Cu4	Cu3	Cu2	113.39(2)	N3	C12	C16B	114.6(8)
N4	Cu3	Cu2	62.08(9)	C11	C12	C16A	124.1(5)
N4	Cu3	Cu4	115.37(10)	C11	C12	C16B	137.5(8)
N4	Cu3	N5	171.38(14)	C10	C13	C14	114.3(4)
N5	Cu3	Cu2	126.30(10)	C10	C13	C15	109.8(4)
N5	Cu3	Cu4	64.72(10)	C15	C13	C14	110.7(4)
Cu3	Cu4	Cu1	66.133(16)	C12	C16A	C17A	111.3(7)
N6	Cu4	Cu1	107.35(10)	C12	C16A	C18A	112.8(9)
N6	Cu4	Cu3	66.19(10)	C17A	C16A	C18A	107.7(10)
N7	Cu4	Cu1	64.15(9)	C12	C16B	C17B	107.2(9)
N7	Cu4	Cu3	106.11(10)	C12	C16B	C18B	110.6(13)
N7	Cu4	N6	170.91(14)	C17B	C16B	C18B	116.2(15)
N2	N1	Cu1	115.4(2)	N6	C19	C20	107.3(3)
C3	N1	Cu1	135.8(3)	N6	C19	C22	122.8(4)
C3	N1	N2	108.5(3)	C20	C19	C22	129.9(4)
N1	N2	Cu2	111.5(2)	C19	C20	Br3	126.7(3)
C1	N2	Cu2	135.3(3)	C19	C20	C21	108.6(3)
C1	N2	N1	108.5(3)	C21	C20	Br3	124.7(3)
N4	N3	Cu2	112.4(2)	N5	C21	C20	107.1(3)
C12	N3	Cu2	138.6(3)	N5	C21	C25	124.0(3)
C12	N3	N4	108.7(3)	C20	C21	C25	128.9(4)
N3	N4	Cu3	119.3(2)	C19	C22	C23	111.8(3)
C10	N4	Cu3	132.3(3)	C19	C22	C24	111.3(3)
C10	N4	N3	108.5(3)	C23	C22	C24	111.8(4)
N6	N5	Cu3	114.4(2)	C21	C25	C26	113.8(3)
C21	N5	Cu3	136.3(3)	C21	C25	C27	109.8(4)
C21	N5	N6	108.3(3)	C27	C25	C26	111.4(4)
N5	N6	Cu4	112.0(2)	N8	C28	C29	107.9(3)

C19	N6	Cu4	138.3(3)	N8	C28	C31	123.4(3)
C19	N6	N5	108.7(3)	C29	C28	C31	128.7(4)
N8	N7	Cu4	114.4(2)	C28	C29	Br4	125.5(3)
C30	N7	Cu4	136.7(3)	C30	C29	Br4	126.7(3)
C30	N7	N8	108.7(3)	C30	C29	C28	107.8(3)
N7	N8	Cu1	116.8(2)	N7	C30	C29	107.4(3)
C28	N8	Cu1	133.8(3)	N7	C30	C34	122.6(9)
C28	N8	N7	108.1(3)	N7	C30	C34A	122.3(5)
N2	C1	C2	107.4(3)	C29	C30	C34	128.5(10)
N2	C1	C4	121.1(3)	C29	C30	C34A	130.2(5)
C2	C1	C4	131.5(4)	C28	C31	C32	113.8(3)
C1	C2	Br1	127.1(3)	C28	C31	C33	110.2(3)
C1	C2	C3	108.0(3)	C32	C31	C33	110.9(4)
C3	C2	Br1	124.8(3)	C30	C34	C35	115.7(15)
N1	C3	C2	107.6(3)	C30	C34	C36	100.7(11)
N1	C3	C7	123.4(3)	C35	C34	C36	108.1(17)
C2	C3	C7	129.0(4)	C30	C34A	C35A	107.1(5)
C1	C4	C5	111.9(3)	C30	C34A	C36A	115.1(5)
C1	C4	C6	112.5(3)	C36A	C34A	C35A	111.2(6)

Table S5. Crystal data and structure refinement for $\{[3,5\text{-}(Pr^{i})_2,4\text{-}(Br)Pz]Cu\}_4$ (276K)**.**

Identification code	dias344s
Empirical formula	$C_{36}H_{56}N_8Cu_4Br_4$
Formula weight	1174.68
Temperature/K	276.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	19.0932(8)
b/Å	21.3451(8)
c/Å	23.1709(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9443.2(6)
Z	8
ρ_{calc}g/cm^3	1.652
μ/mm^{-1}	5.195
F(000)	4672.0
Crystal size/mm^3	0.23 × 0.11 × 0.046
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.816 to 50
Index ranges	$-22 \le h \le 22$, $-25 \le k \le 25$, $-27 \le l \le 27$
Reflections collected	68262
Independent reflections	8319 [R_{int} = 0.0488, R_{sigma} = 0.0284]
Data/restraints/parameters	8319/42/511
Goodness-of-fit on F^2	0.995
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0825
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.0970
Largest diff. peak/hole / e Å^{-3}	0.73/-0.49

Table S6. Bond Lengths for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ (276K).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu2	3.0231(8)	C4	C5	1.476(9)
Cu1	Cu4	2.9361(8)	C4	C6	1.466(9)
Cu1	N1	1.859(3)	C7	C8	1.504(9)
Cu1	N8	1.862(3)	C7	C9	1.489(8)
Cu2	Cu3	2.9509(8)	C10	C11	1.373(6)
Cu2	N2	1.851(4)	C10	C13	1.497(7)
Cu2	N3	1.855(4)	C11	C12	1.376(6)
Cu3	Cu4	3.0029(8)	C12	C16	1.502(6)
Cu3	N4	1.866(3)	C13	C14	1.452(9)
Cu3	N5	1.865(3)	C13	C15	1.508(9)
Cu4	N6	1.842(3)	C16	C17	1.484(8)
Cu4	N7	1.846(3)	C16	C18	1.502(8)
N1	N2	1.388(5)	C19	C20	1.384(6)
N1	C3	1.337(5)	C19	C22A	1.51(2)
N2	C1	1.348(5)	C19	C22B	1.541(15)
N3	N4	1.383(5)	C20	C21	1.382(6)
N3	C12	1.350(5)	C21	C25	1.492(6)
N4	C10	1.353(6)	C22A	C24A	1.502(15)
N5	N6	1.387(5)	C22A	C23A	1.516(15)
N5	C21	1.332(5)	C22B	C24B	1.509(13)
N6	C19	1.337(5)	C22B	C23B	1.505(12)
N7	N8	1.384(5)	C25	C26	1.487(7)
N7	C30	1.344(5)	C25	C27	1.496(9)
N8	C28	1.333(5)	C28	C29	1.381(6)
Br1	C2	1.883(4)	C28	C31	1.500(6)
Br2	C11	1.882(4)	C29	C30	1.377(6)
Br3	C20	1.872(4)	C30	C34	1.508(6)
Br4	C29	1.880(4)	C31	C32	1.518(7)
C1	C2	1.387(6)	C31	C33	1.491(7)
C1	C4	1.484(6)	C34	C35	1.508(7)
C2	C3	1.372(6)	C34	C36	1.511(8)
C3	C7	1.512(7)			

Table S7. Bond Angles for {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$ (276K).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu4	Cu1	Cu2	113.13(2)	C5	C4	C1	112.8(5)
N1	Cu1	Cu2	62.89(11)	C6	C4	C1	112.6(5)
N1	Cu1	Cu4	118.78(12)	C6	C4	C5	113.3(7)
N1	Cu1	N8	174.94(16)	C8	C7	C3	110.5(5)
N8	Cu1	Cu2	120.83(12)	C9	C7	C3	113.5(5)
N8	Cu1	Cu4	63.76(11)	C9	C7	C8	111.6(6)
Cu3	Cu2	Cu1	66.309(19)	N4	C10	C11	107.3(4)
N2	Cu2	Cu1	64.43(11)	N4	C10	C13	123.5(4)
N2	Cu2	Cu3	106.31(12)	C11	C10	C13	129.2(5)
N2	Cu2	N3	170.22(16)	C10	C11	Br2	125.8(4)
N3	Cu2	Cu1	106.39(11)	C10	C11	C12	108.7(4)
N3	Cu2	Cu3	65.48(11)	C12	C11	Br2	125.5(4)
Cu2	Cu3	Cu4	113.29(2)	N3	C12	C11	107.2(4)
N4	Cu3	Cu2	63.79(11)	N3	C12	C16	122.8(4)
N4	Cu3	Cu4	125.11(12)	C11	C12	C16	130.0(4)
N5	Cu3	Cu2	116.94(11)	C10	C13	C15	110.5(5)
N5	Cu3	Cu4	62.39(11)	C14	C13	C10	115.5(5)
N5	Cu3	N4	172.13(16)	C14	C13	C15	119.4(7)
Cu1	Cu4	Cu3	66.753(19)	C17	C16	C12	112.9(4)
N6	Cu4	Cu1	103.53(12)	C17	C16	C18	114.5(5)
N6	Cu4	Cu3	65.83(11)	C18	C16	C12	111.8(5)
N6	Cu4	N7	167.10(16)	N6	C19	C20	107.3(4)
N7	Cu4	Cu1	66.18(11)	N6	C19	C22A	129.2(8)
N7	Cu4	Cu3	102.03(12)	N6	C19	C22B	116.9(7)
N2	N1	Cu1	117.1(3)	C20	C19	C22A	122.7(8)
C3	N1	Cu1	133.5(3)	C20	C19	C22B	135.6(7)
C3	N1	N2	108.5(3)	C19	C20	Br3	126.4(3)
N1	N2	Cu2	114.4(3)	C21	C20	Br3	125.7(3)
C1	N2	Cu2	137.2(3)	C21	C20	C19	107.9(4)
C1	N2	N1	108.3(4)	N5	C21	C20	107.7(4)
N4	N3	Cu2	112.6(3)	N5	C21	C25	123.5(4)
C12	N3	Cu2	137.8(3)	C20	C21	C25	128.7(4)
C12	N3	N4	108.5(4)	C19	C22A	C23A	106.2(17)
N3	N4	Cu3	115.4(3)	C24A	C22A	C19	113.0(15)
C10	N4	Cu3	135.4(3)	C24A	C22A	C23A	98.1(18)
C10	N4	N3	108.3(3)	C24B	C22B	C19	108.6(11)
N6	N5	Cu3	118.6(3)	C23B	C22B	C19	112.6(10)
C21	N5	Cu3	132.9(3)	C23B	C22B	C24B	113.5(12)
C21	N5	N6	108.4(3)	C21	C25	C27	109.6(5)
N5	N6	Cu4	112.9(3)	C26	C25	C21	115.7(5)

C19	N6	Cu4	138.2(3)	C26	C25	C27	111.4(6)
C19	N6	N5	108.7(3)	N8	C28	C29	107.5(4)
N8	N7	Cu4	112.2(2)	N8	C28	C31	123.1(4)
C30	N7	Cu4	135.6(3)	C29	C28	C31	129.3(4)
C30	N7	N8	108.5(3)	C28	C29	Br4	125.2(3)
N7	N8	Cu1	116.1(3)	C30	C29	Br4	126.5(3)
C28	N8	Cu1	135.2(3)	C30	C29	C28	108.3(4)
C28	N8	N7	108.6(3)	N7	C30	C29	107.2(4)
N2	C1	C2	107.0(4)	N7	C30	C34	122.1(4)
N2	C1	C4	123.3(4)	C29	C30	C34	130.7(4)
C2	C1	C4	129.7(4)	C28	C31	C32	113.3(4)
C1	C2	Br1	125.9(3)	C33	C31	C28	110.2(4)
C3	C2	Br1	125.7(4)	C33	C31	C32	112.6(5)
C3	C2	C1	108.4(4)	C30	C34	C36	110.9(4)
N1	C3	C2	107.8(4)	C35	C34	C30	112.8(4)
N1	C3	C7	123.4(4)	C35	C34	C36	110.2(5)
C2	C3	C7	128.8(4)				

Table S8. Crystal data and structure refinement for {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$**.**

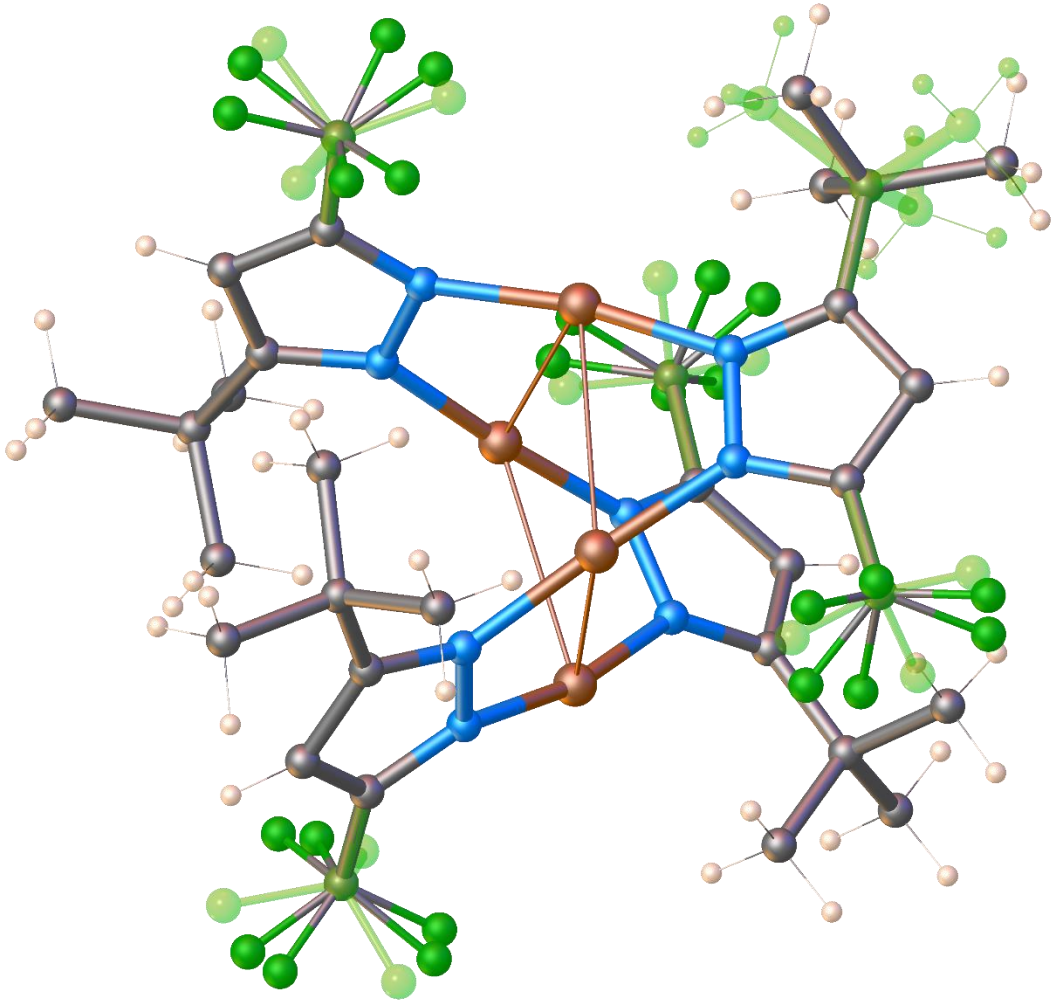


Figure S13. A view of symmetric unit of{[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ and disordered atoms.

Identification code	dias158t
Empirical formula	$C_{32}H_{40}Cu_4F_{12}N_8$
Formula weight	1018.88
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.7771(4)
b/Å	11.5138(4)
c/Å	18.9800(7)
α/°	90.2780(10)
β/°	92.8550(10)
γ/°	107.1450(10)

Volume/Å^3	2038.70(13)
Z	2
ρ_{calc}g/cm^3	1.660
μ/mm^{-1}	2.147
F(000)	1024.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.702 to 55.006
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	27043
Independent reflections	27043 [R_{int} = 0.0315, R_{sigma} = 0.0670]
Data/restraints/parameters	27043/1976/615
Goodness-of-fit on F^2	0.991
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0784, wR_2 = 0.1263
Largest diff. peak/hole / e Å^{-3}	2.05/-0.55

Table S9. Bond Lengths for {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu2	2.9514(9)	C12	C13	1.511(7)
Cu1	Cu4	3.0065(9)	C13	C14	1.507(8)
Cu1	N1	1.850(5)	C13	C15	1.529(8)
Cu1	N8	1.856(4)	C13	C16	1.526(8)
Cu2	Cu3	3.0204(9)	N5	N6	1.383(6)
Cu2	N2	1.864(4)	N5	C18	1.338(7)
Cu2	N3	1.866(4)	N6	C20	1.352(6)
Cu3	Cu4	2.9146(9)	C17	F7	1.357(9)
Cu3	N4	1.864(4)	C17	F8	1.369(10)
Cu3	N5	1.858(5)	C17	F9	1.349(9)
Cu4	N6	1.860(4)	C17	C18	1.479(8)
Cu4	N7	1.862(5)	C17'	F7'	1.34(2)
N1	N2	1.385(6)	C17'	F8'	1.32(2)
N1	C2	1.338(7)	C17'	F9'	1.35(2)
N2	C4	1.346(6)	C17'	C18	1.479(8)
C1	F1	1.346(8)	C17"	F7"	1.357(19)
C1	F2	1.354(8)	C17"	F8"	1.349(19)
C1	F3	1.347(8)	C17"	F9"	1.329(19)
C1	C2	1.485(8)	C17"	C18	1.479(8)
C1'	F1'	1.33(2)	C18	C19	1.379(7)
C1'	F2'	1.34(2)	C19	C20	1.394(7)
C1'	F3'	1.35(2)	C20	C21	1.521(7)
C1'	C2	1.485(8)	C21	C22	1.522(8)
C1"	F1"	1.35(2)	C21	C23	1.516(8)
C1"	F2"	1.34(2)	C21	C24	1.531(8)
C1"	F3"	1.35(2)	N7	N8	1.368(6)
C1"	C2	1.485(8)	N7	C26	1.348(7)
C2	C3	1.384(8)	N8	C28	1.349(6)
C3	C4	1.379(7)	C25	F10	1.303(17)
C4	C5	1.524(7)	C25	F11	1.379(14)
C5	C6	1.527(8)	C25	F12	1.368(17)
C5	C7	1.535(8)	C25	C26	1.482(8)
C5	C8	1.534(8)	C25'	F10'	1.364(16)
N3	N4	1.365(6)	C25'	F11'	1.354(13)
N3	C10	1.336(7)	C25'	F12'	1.329(15)
N4	C12	1.350(6)	C25'	C26	1.482(8)
C9	F4	1.349(9)	C25"	F10"	1.34(2)
C9	F5	1.347(9)	C25"	F11"	1.38(2)
C9	F6	1.356(9)	C25"	F12"	1.34(2)
C9	C10	1.490(8)	C25"	C26	1.482(8)

C9'	F4'	1.330(19)	C26	C27	1.378(8)
C9'	F5'	1.349(19)	C27	C28	1.391(7)
C9'	F6'	1.351(19)	C28	C29	1.521(7)
C9'	C10	1.490(8)	C28	C29'	1.521(7)
C9"	F4"	1.33(2)	C29	C30	1.536(11)
C9"	F5"	1.38(2)	C29	C31	1.512(10)
C9"	F6"	1.34(2)	C29	C32	1.535(10)
C9"	C10	1.490(8)	C29'	C30'	1.47(2)
C10	C11	1.375(8)	C29'	C31'	1.53(2)
C11	C12	1.386(7)	C29'	C32'	1.59(2)

Table S10. Bond Angles for {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cu2	Cu1	Cu4	79.76(2)	N4	C12	C13	122.6(5)
N1	Cu1	Cu2	65.05(14)	C11	C12	C13	128.6(5)
N1	Cu1	Cu4	105.44(15)	C12	C13	C15	109.3(5)
N1	Cu1	N8	170.1(2)	C12	C13	C16	108.0(5)
N8	Cu1	Cu2	109.85(14)	C14	C13	C12	112.8(5)
N8	Cu1	Cu4	64.81(13)	C14	C13	C15	108.5(6)
Cu1	Cu2	Cu3	98.01(3)	C14	C13	C16	109.1(5)
N2	Cu2	Cu1	64.54(13)	C16	C13	C15	109.1(6)
N2	Cu2	Cu3	119.04(14)	N6	N5	Cu3	113.0(3)
N2	Cu2	N3	175.75(19)	C18	N5	Cu3	138.5(4)
N3	Cu2	Cu1	111.53(14)	C18	N5	N6	106.8(4)
N3	Cu2	Cu3	62.33(14)	N5	N6	Cu4	114.4(3)
Cu4	Cu3	Cu2	80.11(2)	C20	N6	Cu4	136.8(4)
N4	Cu3	Cu2	64.60(13)	C20	N6	N5	108.7(4)
N4	Cu3	Cu4	109.85(14)	F7	C17	F8	104.5(6)
N5	Cu3	Cu2	104.71(15)	F7	C17	C18	113.3(6)
N5	Cu3	Cu4	65.76(14)	F8	C17	C18	113.1(8)
N5	Cu3	N4	169.3(2)	F9	C17	F7	106.1(6)
Cu3	Cu4	Cu1	99.14(3)	F9	C17	F8	106.5(7)
N6	Cu4	Cu1	118.09(14)	F9	C17	C18	112.8(7)
N6	Cu4	Cu3	65.02(13)	F7'	C17'	F9'	104(2)
N6	Cu4	N7	175.15(19)	F7'	C17'	C18	115(3)
N7	Cu4	Cu1	62.76(14)	F8'	C17'	F7'	111(2)
N7	Cu4	Cu3	110.23(14)	F8'	C17'	F9'	109(2)
N2	N1	Cu1	114.4(3)	F8'	C17'	C18	110(2)
C2	N1	Cu1	138.1(4)	F9'	C17'	C18	107(2)
C2	N1	N2	106.3(4)	F7"	C17"	C18	109.4(17)
N1	N2	Cu2	114.5(3)	F8"	C17"	F7"	106.2(16)
C4	N2	Cu2	136.7(4)	F8"	C17"	C18	113.3(19)
C4	N2	N1	108.7(4)	F9"	C17"	F7"	109.9(17)
F1	C1	F2	106.1(6)	F9"	C17"	F8"	107.5(19)
F1	C1	F3	105.8(6)	F9"	C17"	C18	110.5(17)
F1	C1	C2	111.9(7)	N5	C18	C17	120.2(5)
F2	C1	C2	112.5(6)	N5	C18	C17'	120.2(5)
F3	C1	F2	105.3(6)	N5	C18	C17"	120.2(5)
F3	C1	C2	114.6(6)	N5	C18	C19	110.8(5)
F1'	C1'	F2'	107(2)	C19	C18	C17	129.0(5)
F1'	C1'	F3'	106(2)	C19	C18	C17'	129.0(5)
F1'	C1'	C2	112(3)	C19	C18	C17"	129.0(5)
F2'	C1'	F3'	110(2)	C18	C19	C20	105.2(5)

F2'	C1'	C2	113(2)	N6	C20	C19	108.5(4)
F3'	C1'	C2	108.5(17)	N6	C20	C21	121.1(5)
F1"	C1"	F3"	106(2)	C19	C20	C21	130.3(5)
F1"	C1"	C2	109.0(19)	C20	C21	C22	109.9(5)
F2"	C1"	F1"	108(2)	C20	C21	C24	109.4(5)
F2"	C1"	F3"	107(2)	C22	C21	C24	108.6(5)
F2"	C1"	C2	114.4(19)	C23	C21	C20	108.9(5)
F3"	C1"	C2	111(2)	C23	C21	C22	110.6(5)
N1	C2	C1	121.0(5)	C23	C21	C24	109.4(5)
N1	C2	C1'	121.0(5)	N8	N7	Cu4	118.0(3)
N1	C2	C1"	121.0(5)	C26	N7	Cu4	134.1(4)
N1	C2	C3	110.9(5)	C26	N7	N8	107.7(5)
C3	C2	C1	128.1(5)	N7	N8	Cu1	114.0(3)
C3	C2	C1'	128.1(5)	C28	N8	Cu1	137.4(4)
C3	C2	C1"	128.1(5)	C28	N8	N7	108.5(4)
C4	C3	C2	104.9(5)	F10	C25	F11	108.4(12)
N2	C4	C3	109.2(5)	F10	C25	F12	106.4(15)
N2	C4	C5	120.5(5)	F10	C25	C26	114.3(15)
C3	C4	C5	130.3(5)	F11	C25	C26	112.7(9)
C4	C5	C6	110.3(5)	F12	C25	F11	104.6(10)
C4	C5	C7	109.5(5)	F12	C25	C26	109.7(13)
C4	C5	C8	109.7(5)	F10'	C25'	C26	110.1(11)
C6	C5	C7	109.7(5)	F11'	C25'	F10'	105.1(9)
C6	C5	C8	109.2(5)	F11'	C25'	C26	111.2(8)
C8	C5	C7	108.5(5)	F12'	C25'	F10'	107.6(11)
N4	N3	Cu2	118.4(3)	F12'	C25'	F11'	108.8(9)
C10	N3	Cu2	134.4(4)	F12'	C25'	C26	113.6(10)
C10	N3	N4	106.9(4)	F10"	C25"	F11"	103(2)
N3	N4	Cu3	113.5(3)	F10"	C25"	C26	115.6(17)
C12	N4	Cu3	137.1(4)	F11"	C25"	C26	112.5(18)
C12	N4	N3	108.8(4)	F12"	C25"	F10"	105(2)
F4	C9	F6	106.5(6)	F12"	C25"	F11"	107(2)
F4	C9	C10	111.8(6)	F12"	C25"	C26	112.5(15)
F5	C9	F4	106.1(6)	N7	C26	C25	120.7(5)
F5	C9	F6	106.7(7)	N7	C26	C25'	120.7(5)
F5	C9	C10	113.0(7)	N7	C26	C25"	120.7(5)
F6	C9	C10	112.2(6)	N7	C26	C27	109.5(5)
F4'	C9'	F5'	108.5(18)	C27	C26	C25	129.8(5)
F4'	C9'	F6'	106.7(16)	C27	C26	C25'	129.8(5)
F4'	C9'	C10	111.7(17)	C27	C26	C25"	129.8(5)
F5'	C9'	F6'	104.8(17)	C26	C27	C28	105.7(5)
F5'	C9'	C10	113.9(17)	N8	C28	C27	108.6(5)

F6'	C9'	C10	110.7(15)	N8	C28	C29	121.6(5)
F4"	C9"	F5"	105(2)	N8	C28	C29'	121.6(5)
F4"	C9"	F6"	107(2)	C27	C28	C29	129.8(5)
F4"	C9"	C10	115(2)	C27	C28	C29'	129.8(5)
F5"	C9"	C10	107.5(19)	C28	C29	C30	109.7(6)
F6"	C9"	F5"	106(2)	C28	C29	C32	110.0(6)
F6"	C9"	C10	116.2(18)	C31	C29	C28	108.2(6)
N3	C10	C9	120.1(5)	C31	C29	C30	109.4(8)
N3	C10	C9'	120.1(5)	C31	C29	C32	112.3(7)
N3	C10	C9"	120.1(5)	C32	C29	C30	107.2(7)
N3	C10	C11	110.9(5)	C28	C29'	C31'	112.9(13)
C11	C10	C9	129.0(5)	C28	C29'	C32'	106.0(11)
C11	C10	C9'	129.0(5)	C30'	C29'	C28	107.0(12)
C11	C10	C9"	129.0(5)	C30'	C29'	C31'	113.7(17)
C10	C11	C12	104.8(5)	C30'	C29'	C32'	111.2(17)
N4	C12	C11	108.6(5)	C31'	C29'	C32'	105.8(17)

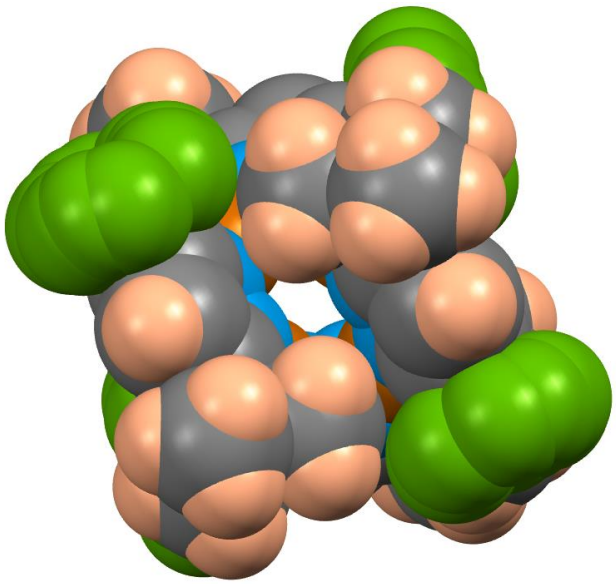
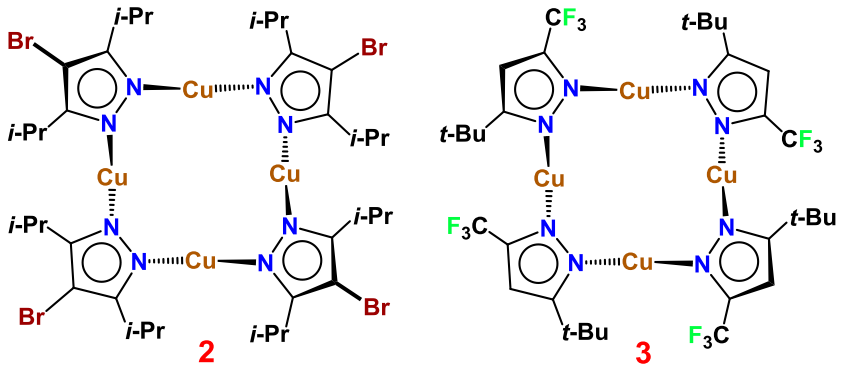


Figure S14. Space-fill diagram of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$.

Table S11. Photoluminescence data for solid samples of complexes {[3,5-(Pr^i)$_2$,4-(Br)Pz]Cu}$_4$, **2** and {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$, **3**.



Complexes	Excitation λ_{max} (nm)	Emission λ_{max} (nm)	$\tau_{4K/298K}$ (μs)	$\Phi_{4K/298K}$
Complex **2**	290	560	653.1/18.7	1.00/0.77
Complex **3**	290	530	453.3/28.9	0.94/0.81

Figure S15. ^{1}H NMR spectrum of {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ **(2)** in $CDCl_3$ at room temperature.

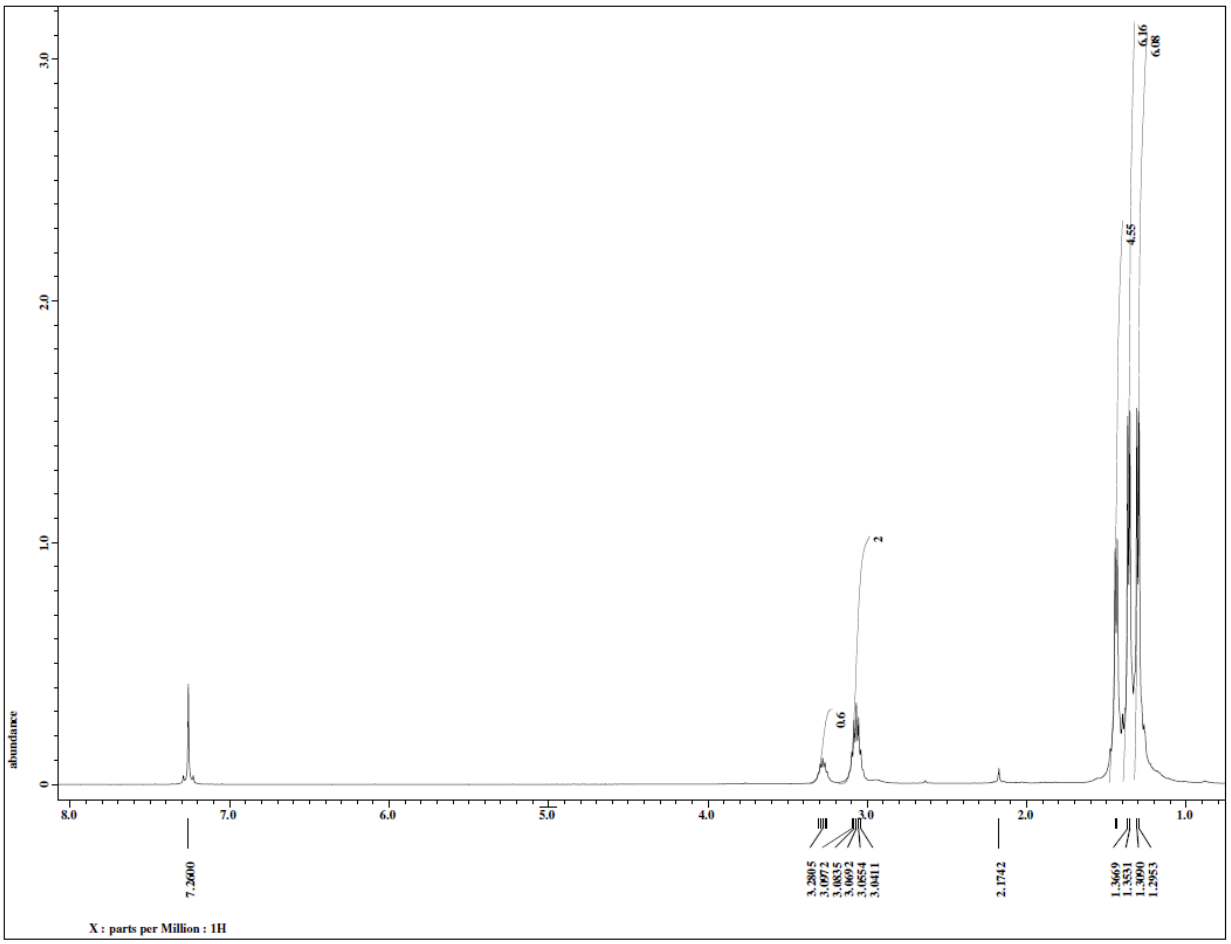
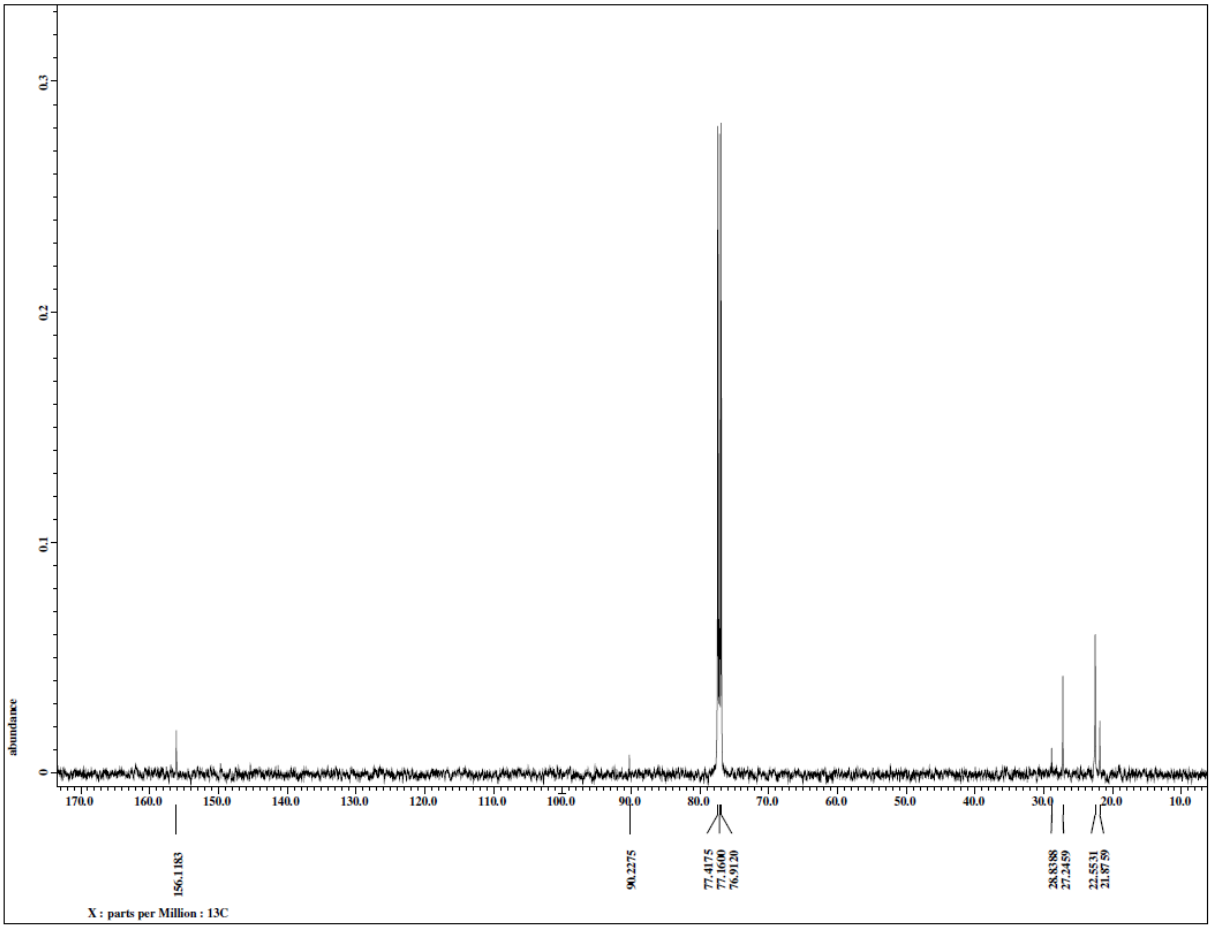


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of $\{[3,5\text{-}(i\text{-}Pr)_2,4\text{-}(Br)Pz]Cu\}_4$ **(2)** in $CDCl_3$ at room temperature



Concentration effect on {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ **(2) (Figures S17 and 18):**

Figure S17. ^{1}H NMR spectrum of 2.27x10^{-3} M {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ **(2)** in $CDCl_3$ at room temperature.

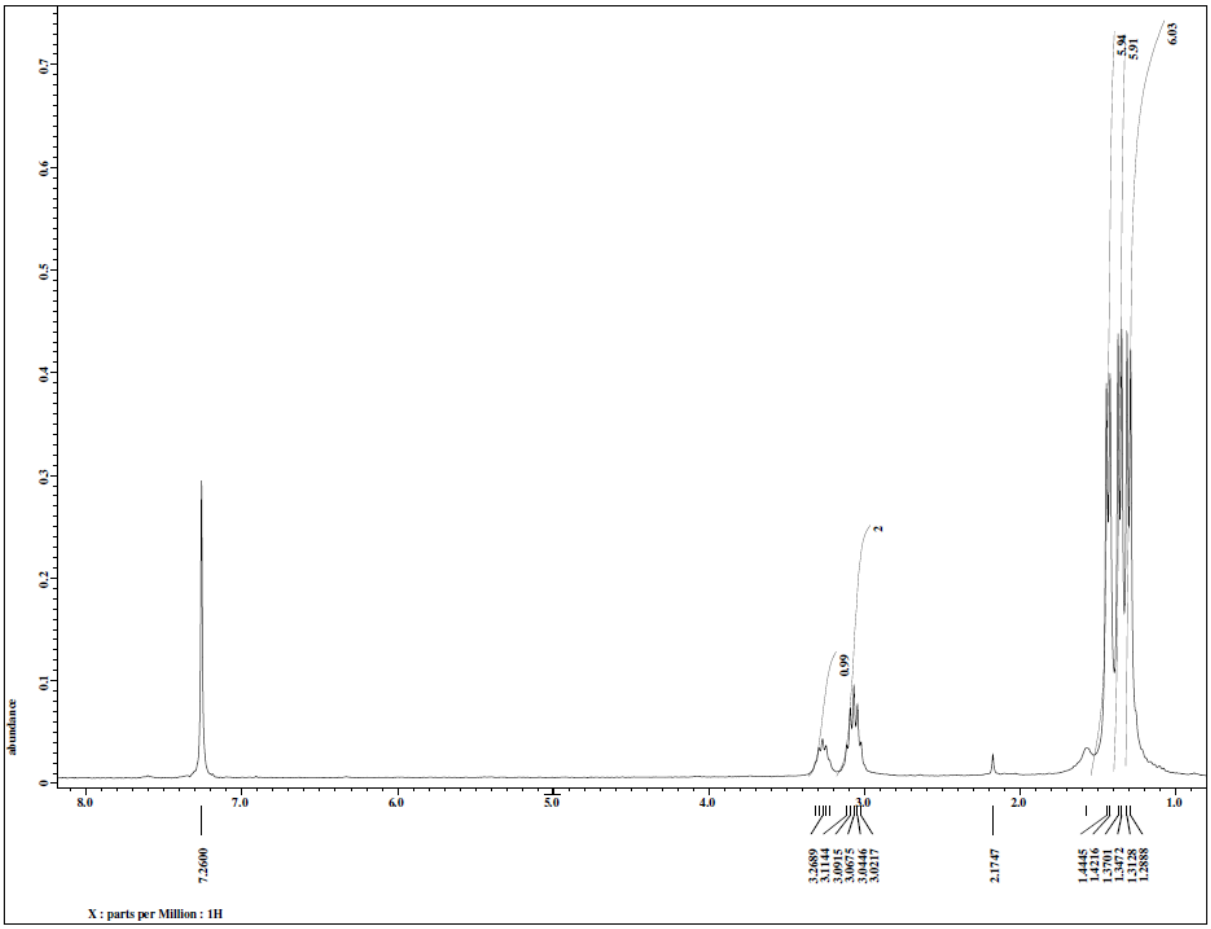


Figure S18. ^{1}H NMR spectrum of 17.0x10^{-3}M {[3,5-(*i*-Pr)$_2$,4-(Br)Pz]Cu}$_4$ **(2)** in $CDCl_3$ at room temperature.

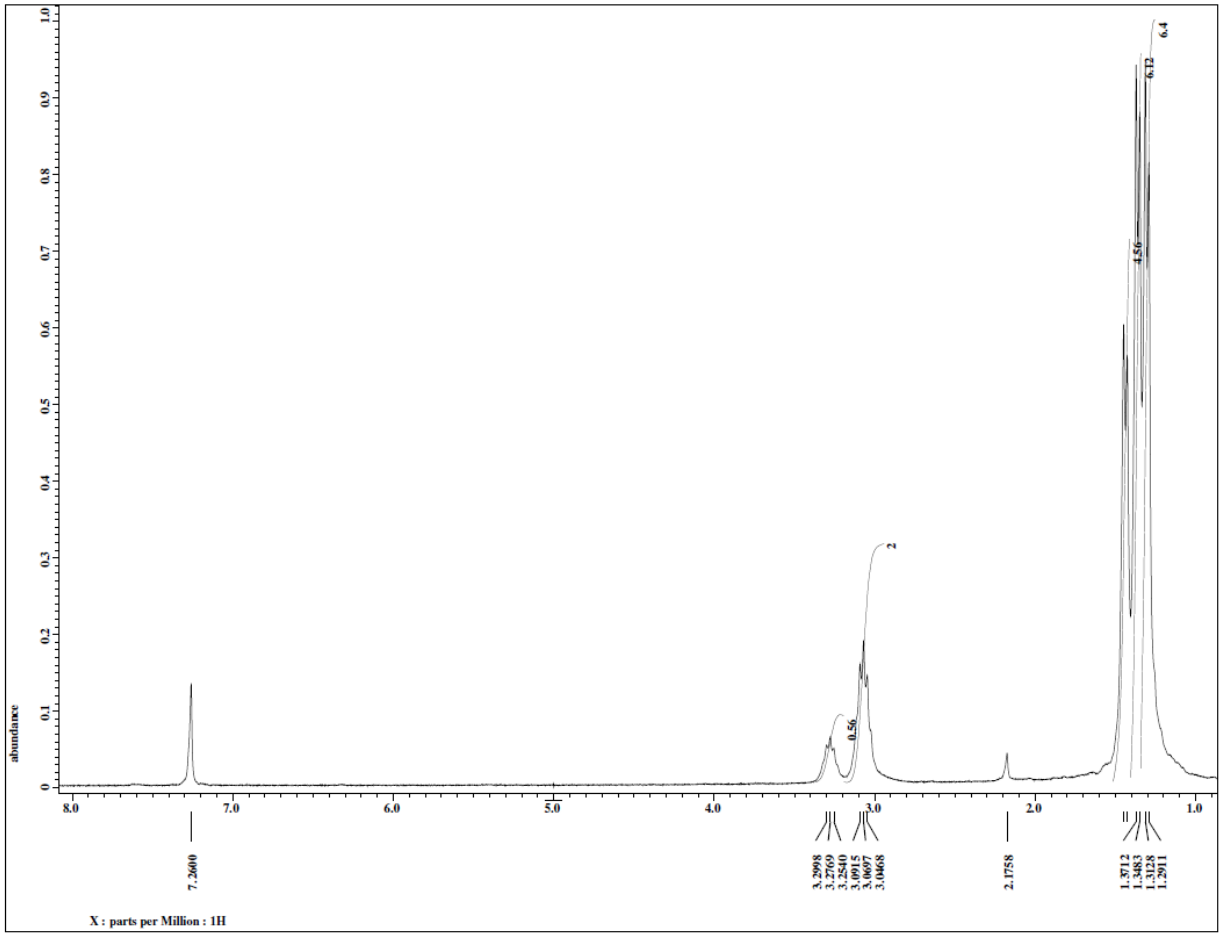


Figure S19. ^{1}H NMR spectrum of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3)** in $CDCl_3$ at room temperature.

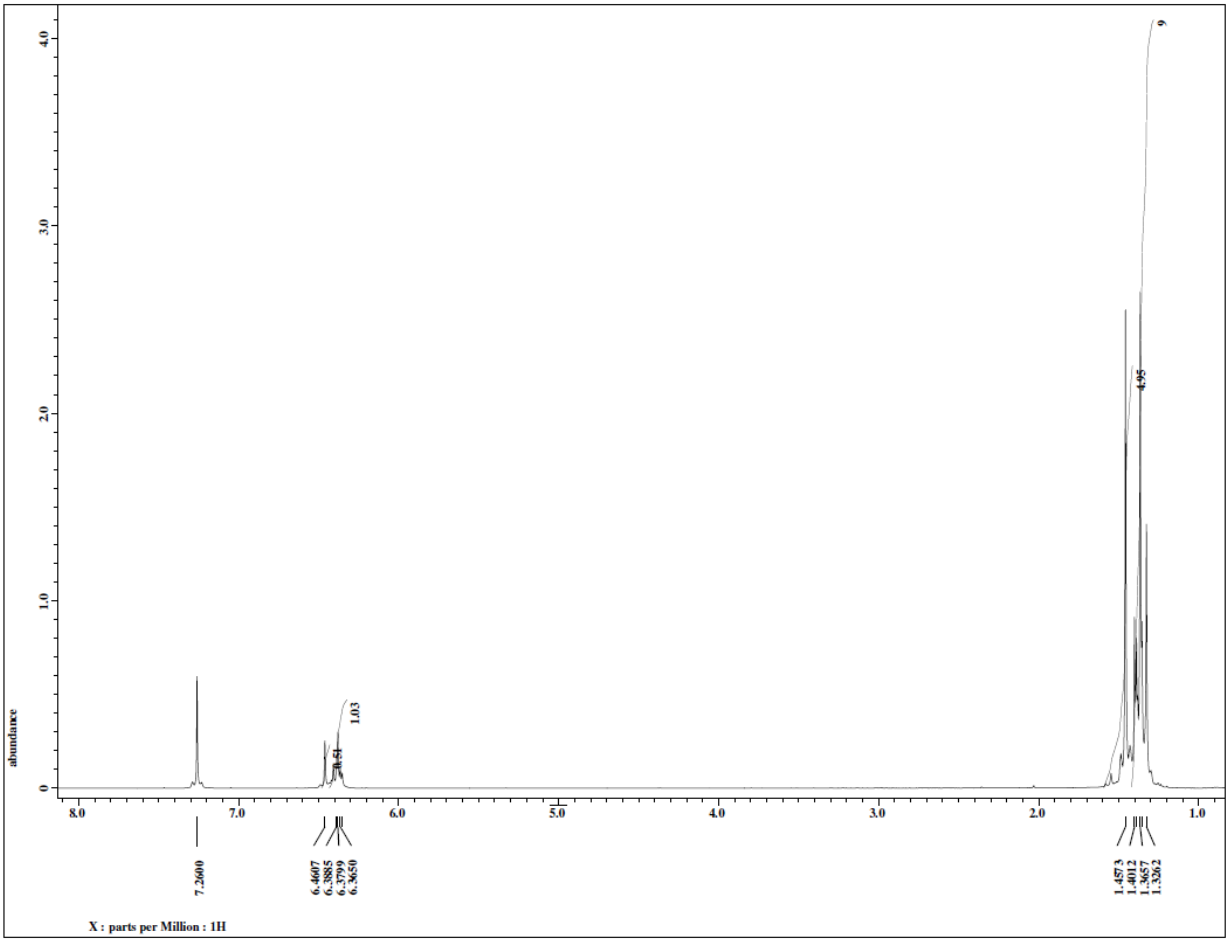


Figure S20. ^{19}F NMR spectrum of {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3)** in C_6D_6 at room temperature.

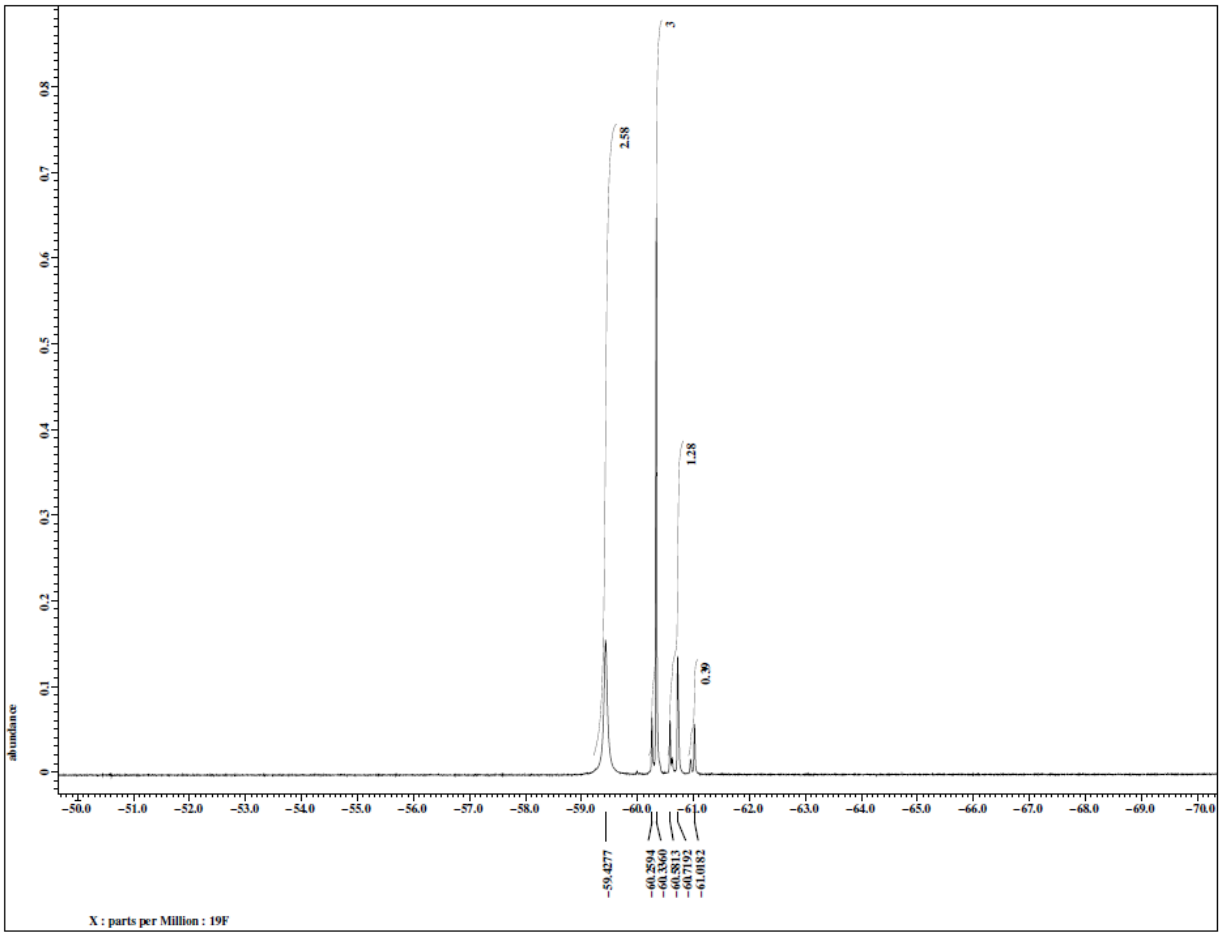
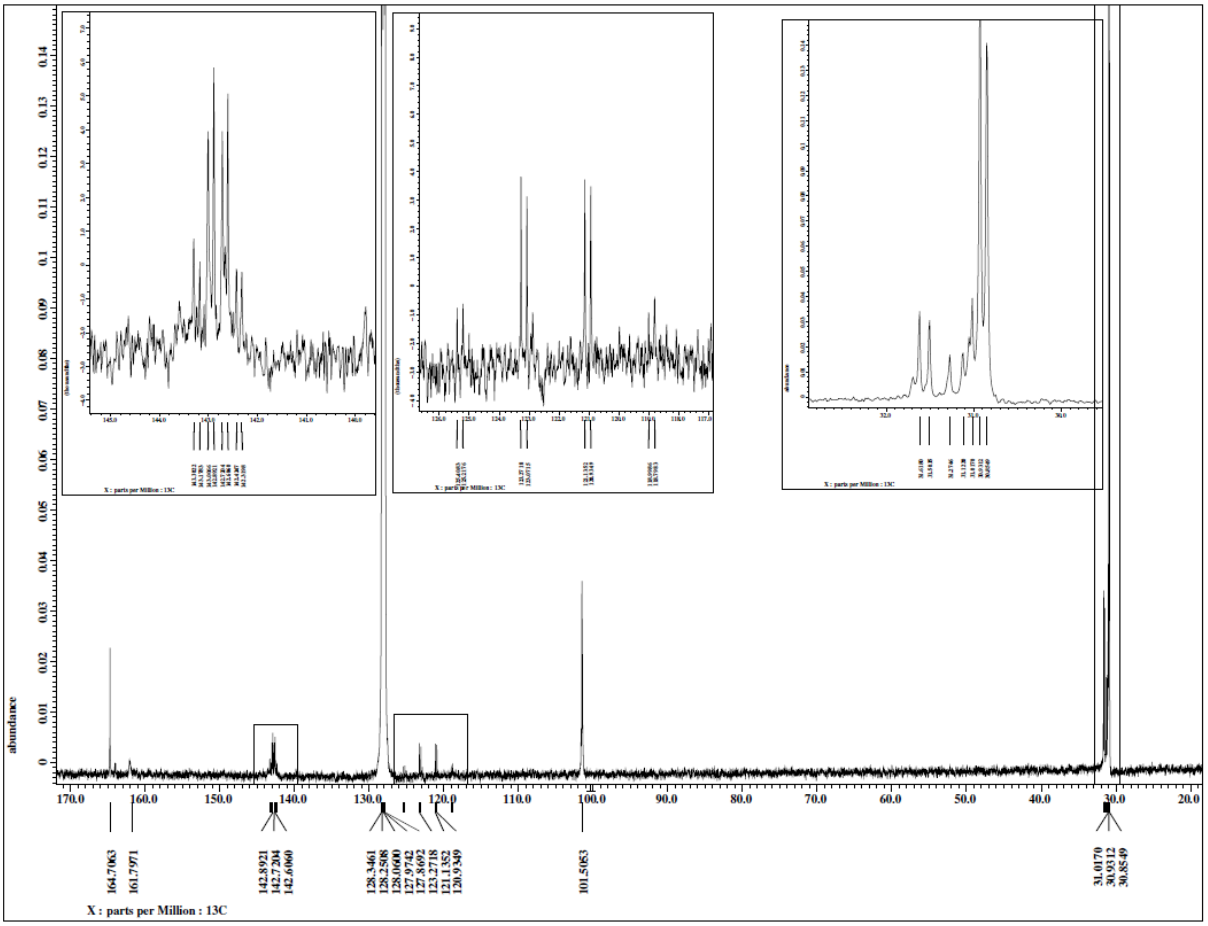


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of $\{[3\text{-}(CF_3),5\text{-}(Bu^t)Pz]Cu\}_4$ **(3)** in C_6D_6 at room temperature.



Concentration effect on {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3) (Figures S22 and 25):**

Figure S22. ^{1}H NMR spectrum of 3.27x10^{-3} M {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3)** in C_6D_6 at room temperature.

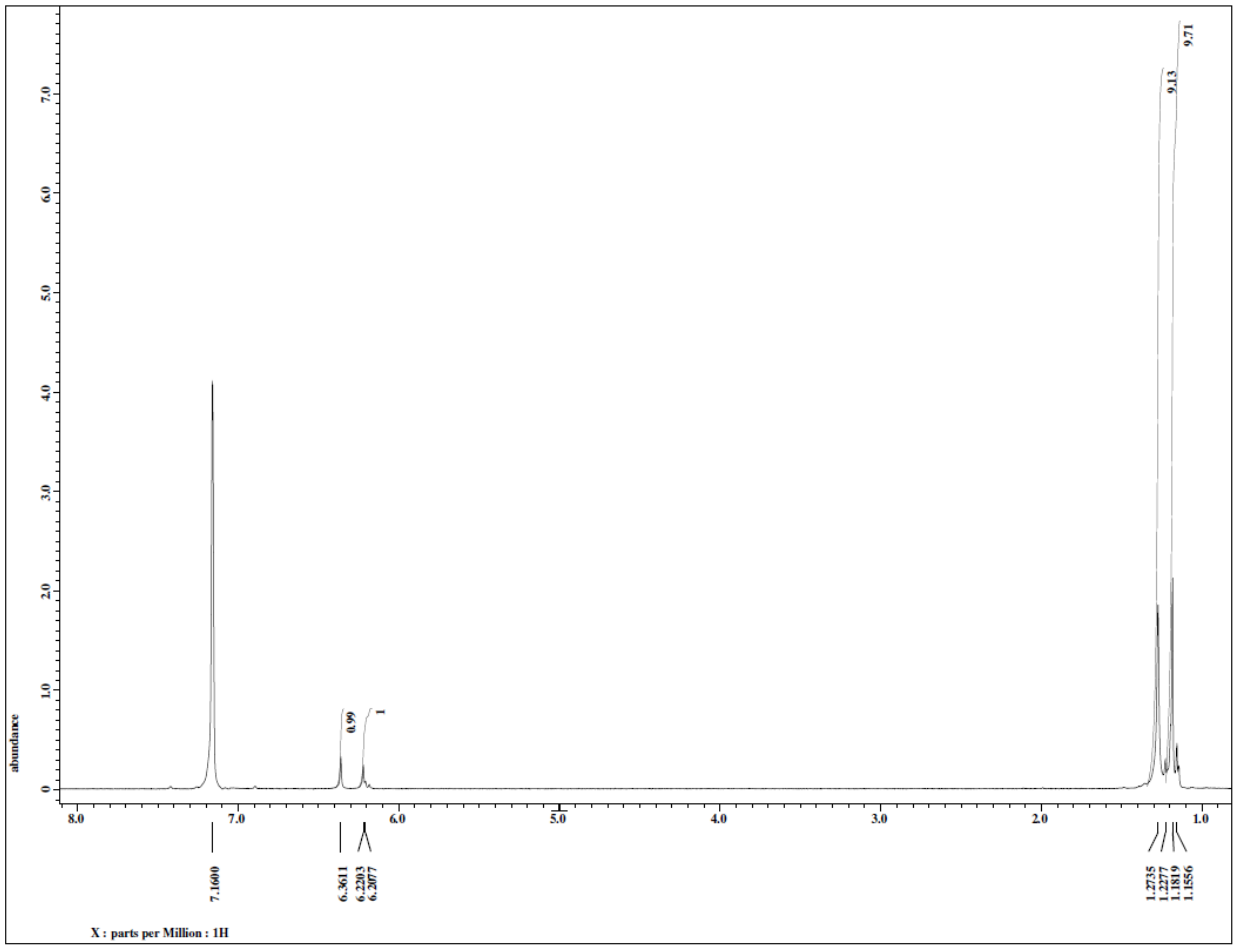


Figure S23. ^{19}F NMR spectrum of $3.27x10^{-3}$ M {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3)** in C_6D_6 at room temperature.

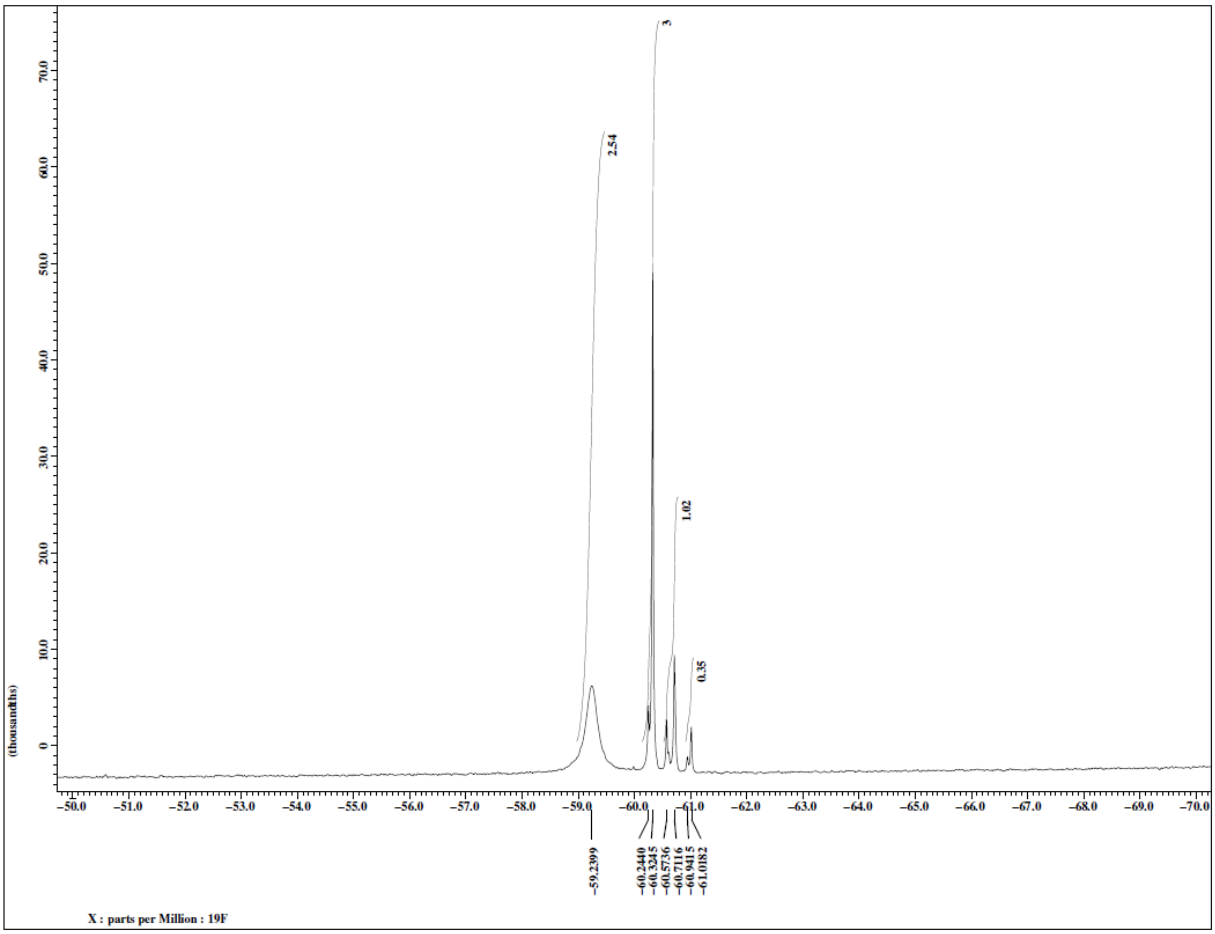


Figure S24. ^{1}H NMR spectrum of $24.5x10^{-3}$ M $\{[3\text{-}(CF_3),5\text{-}(Bu^t)Pz]Cu\}_4$ **(3)** in C_6D_6 at room temperature

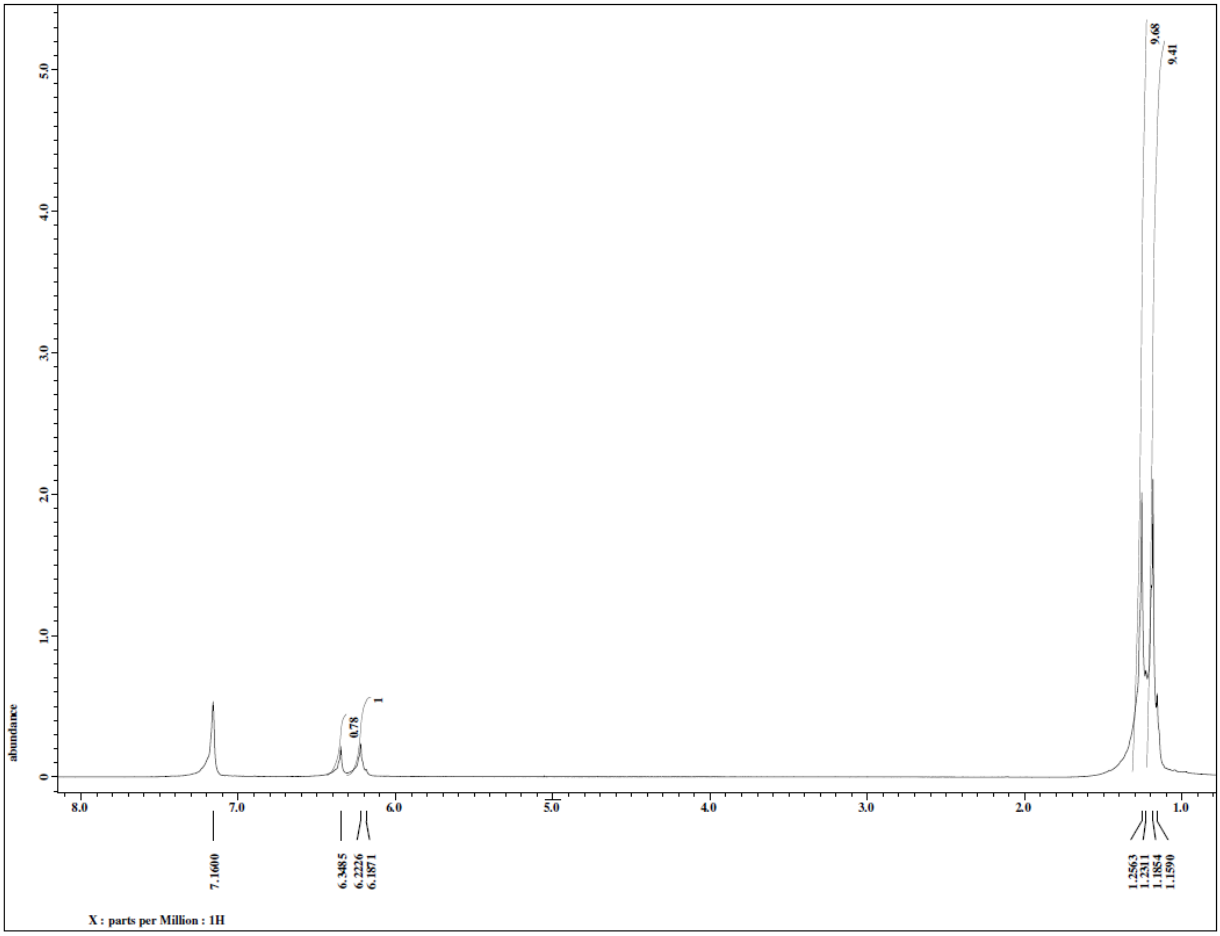
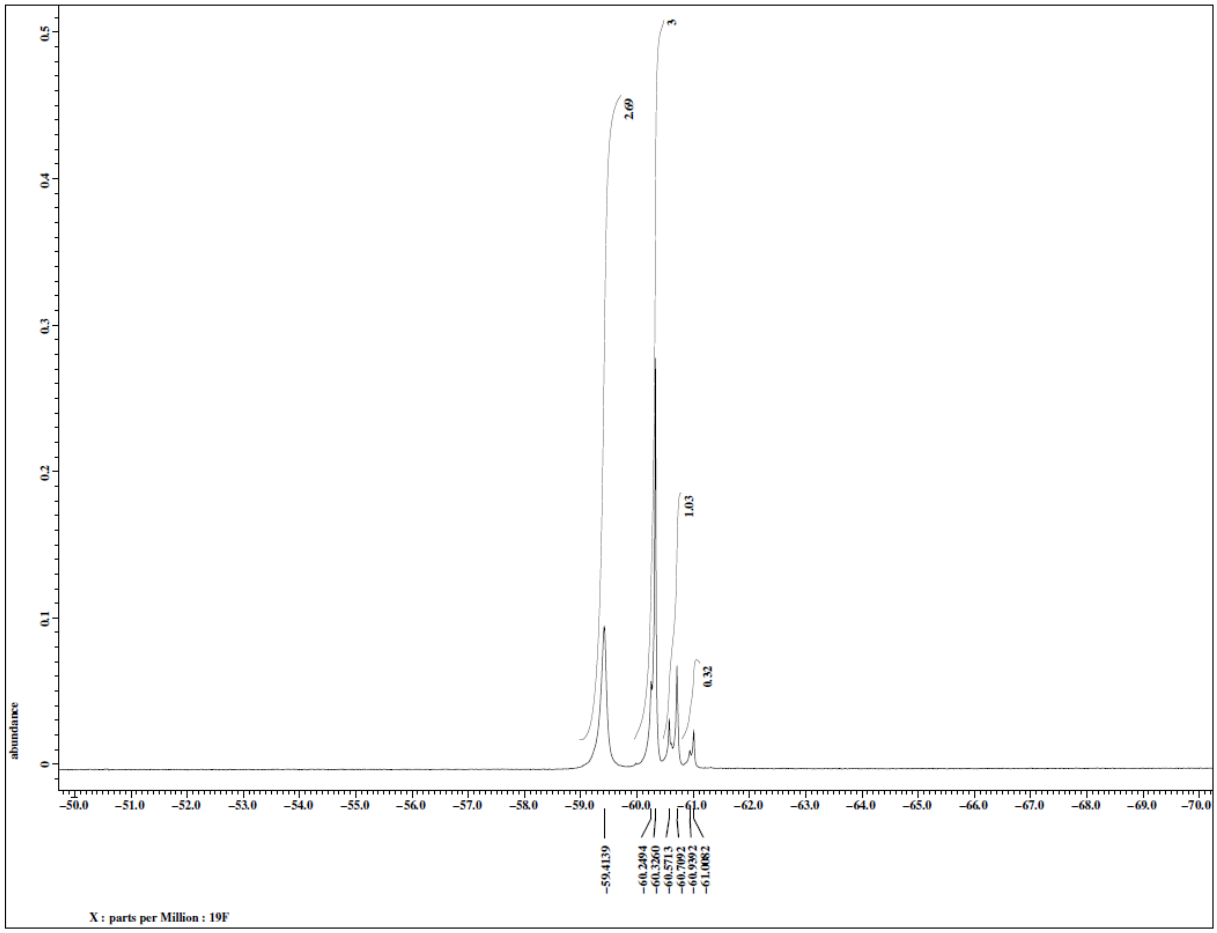


Figure S25. ^{19}F NMR spectrum of $24.5x10^{-3}$ M {[3-(CF_3),5-(Bu^t)Pz]Cu}$_4$ **(3)** in C_6D_6 at room temperature.



References

[1] Y. Takahashi, M. Akita, S. Hikichi, Y. Moro-oka, *Organometallics* **1998**, *17*, 4884-4888.
[2] K. N. Zelenin, V. V. Alekseyev, A. R. Tygysheva, S. I. Yakimovitch, *Tetrahedron* **1995**, *51*, 11251-11256.
[3] G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv.* **2015**, *71*, 3-8.
[4] G. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem.* **2015**, *71*, 3-8.
[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
[6] G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, M. Moret, *Inorg. Chem.* **1994**, *33*, 1458-1463.
[7] A. Maspero, S. Brenna, S. Galli, A. Penoni, *J. Organomet. Chem.* **2003**, *672*, 123-129.
[8] K. Fujisawa, Y. Ishikawa, Y. Miyashita, K.-i. Okamoto, *Inorg. Chim. Acta* **2010**, *363*, 2977-2989.
[9] F. Kiyoshi, I. Yoko, M. Yoshitaro, O. Ken-ichi, *Chem. Lett.* **2004**, *33*, 66-67.
[10] A. A. Titov, A. F. Smol´yakov, A. N. Rodionov, I. D. Kosenko, E. A. Guseva, Y. V. Zubavichus, P. V. Dorovatovskii, O. A. Filippov, E. S. Shubina, *Russ. Chem. Bull.* **2017**, *66*, 1563-1568.