Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Isolable arene sandwiched copper(I) pyrazolates

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Supporting Information

General procedures

Solvents were purchased from commercial sources, dried with molecular sieves prior to use. NMR spectra were recorded on a JEOL Eclipse 500 spectrometer (^{1}H, 500.16 MHz; ^{13}C, 125.77 MHz, ^{19}F, 470.62). Proton and carbon chemical shifts are reported in ppm, and referenced using the residual proton or carbon signals of the deuterated solvent. Fluorine chemical shifts are reported in ppm, and referenced externally to a neat $CFCl_3$. Elemental analyses were performed at Intertek QTI laboratory (Whitehouse, NJ). Melting points were obtained on a Mel-Temp II apparatus. Naphthalene was purchased from Alfa Acer and used without further purification. $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ **[Cu$_3$]** was prepared as reported previously.[1]

(1) Dias, H. V. R.; Polach, S. A.; Wang, Z. *J. Fluor. Chem.* **2000**, *103*, 163-169.

{[Bz][Cu$_3$]$_2$}$_\infty$: $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ **[Cu$_3$]** (100 mg, 0.125 mmol) was dissolved in 1 mL of benzene **[Bz]** and 0.5 mL of $CDCl_3$ was added. The solution was kept at -20 °C to obtain X-ray quality colorless crystals of **{[Bz][Cu$_3$]$_2$}$_\infty$**. Crystals were separated from mother liquor and immediately covered with a layer of hydrocarbon/Paratone-N oil and used for X-ray crystallography. Crystals used in NMR spectroscopy were dried under reduced pressure for about 30 mins at room temperature. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.03 (s), 7.36 (s). ^{19}F NMR

($CDCl_3$): δ (ppm) -61.0 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 104.5 (s, *C*H), 120.0 (q, $^1J(C,F)$ = 269.1 Hz, *C*F_3), 128.5 (s, *C*H, *C*$_6H_6$), 144.6 (m, *C*CF_3). ^1H NMR signal integration indicated the presence of 6.4% benzene in dried sample. Data from elemental analysis agree with the calculated values for **[Cu$_3$]** containing traces of benzene. This observation is consistent with NMR data and indicates the loss of benzene under reduced pressure. Mp: 199-202 ^oC (decomposition). Anal. Calc. for **{[Bz][Cu$_3$]$_2$}$_\infty$**, $C_{36}H_{12}N_{12}Cu_6F_{36}$: C, 25.77; H, 0.72; N, 10.02; Anal. Calc. for **[Cu$_3$]**, $C_{15}H_3N_6Cu_3F_{18}$: C, 22.52; H, 0.38; N, 10.51; Found: C, 22.45; H, 0.25; N, 10.56 (indicates the loss of most benzene and the presence of **[Cu$_3$]** with about 6% benzene).

{[Mes][Cu$_3$]}$_\infty$: [Cu$_3$] (100 mg, 0.125 mmol) was dissolved in 1mL of mesitylene **[Mes]** and 4 mL of $CDCl_3$ was added. The solution was kept at -20 °C to obtain X-ray quality colorless crystals of **{[Mes][Cu$_3$]}$_\infty$.** Crystals were separated from mother liquor and immediately covered with a layer of hydrocarbon/Paratone-N oil and used for X-ray crystallography. Crystals used in NMR spectroscopy were air dried for few mins at room temperature. ^1H NMR ($CDCl_3$): δ (ppm) 2.27 (s), 6.80 (s), 7.02 (s). ^{19}F NMR ($CDCl_3$): δ (ppm) -61.0 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 104.5 (s, *C*H), 120.0 (q, $^1J(C,F)$ = 269.1 Hz, *C*F_3), 127.06 (s, *C*H, *C*$_9H_{12}$), 137.92 (s, *C*CH_3, *C*$_9H_{12}$), 144.6 (q, $^2J(C,F)$ = 38.0 Hz, *C*CF_3). Anal. Calc. for $C_{24}H_{15}N_6Cu_3F_{18}$: C, 31.33; H, 1.64; N, 9.13; Found: C, 32.07; H, 1.70; N, 9.35. M.p. of sample shows two melting temperature events, first partial melting at 126-130 °C and second melting process at 188-192 °C.

{[Nap][Cu$_3$]}$_\infty$: [Cu$_3$] (200 mg, 0.25 mmol) and naphthalene **[Nap]** (32 mg, 0.25 mmol) were dissolved in 1.5 mL of benzene and 1.5 mL of $CDCl_3$ was added. The solution was kept at -20 °C to obtain X-ray quality colorless crystals of **{[Nap][Cu$_3$]}$_\infty$.** Crystals were separated from mother liquor and immediately covered with a layer of hydrocarbon/Paratone-N oil and used for

X-ray crystallography. Crystals used in NMR spectroscopy were dried under reduced pressure for 2 h at room temperature. Anal. Calc. for $C_{25}H_{11}N_6Cu_3F_{18}$: C, 32.36; H, 1.19; N, 9.06; Found: C, 31.88; H, 0.44; N, 9.49. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.02 (s), 7.40 (m), 7.76 (m). ^{19}F NMR ($CDCl_3$): δ (ppm) -61.0 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ (ppm) 104.4 (s, *C*H), 120.0 (q, $^{1}J(C,F)$ = 269.1 Hz, *C*F_3), 126.06 (s, *C*H, Nap), 128.0 (s, *C*H, Nap), 133.5 (s, *C*-CH, Nap), 144.4 (q, $^{2}J(C,F)$ = 38.0 Hz, *C*CF_3).

Photophysical measurements: Steady state luminescence spectra were acquired using a Horiba J-Y Fluoromax 3 with upgrades for lifetime fluorescence studies. The excitation and emission spectra were corrected using factors supplied by the manufacturer. Solid samples were placed in a solid sample cell and covered with a quarts plate for measurements. Photophysical data of arene free **[Cu_3]** has been reported (see: H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489-7501).

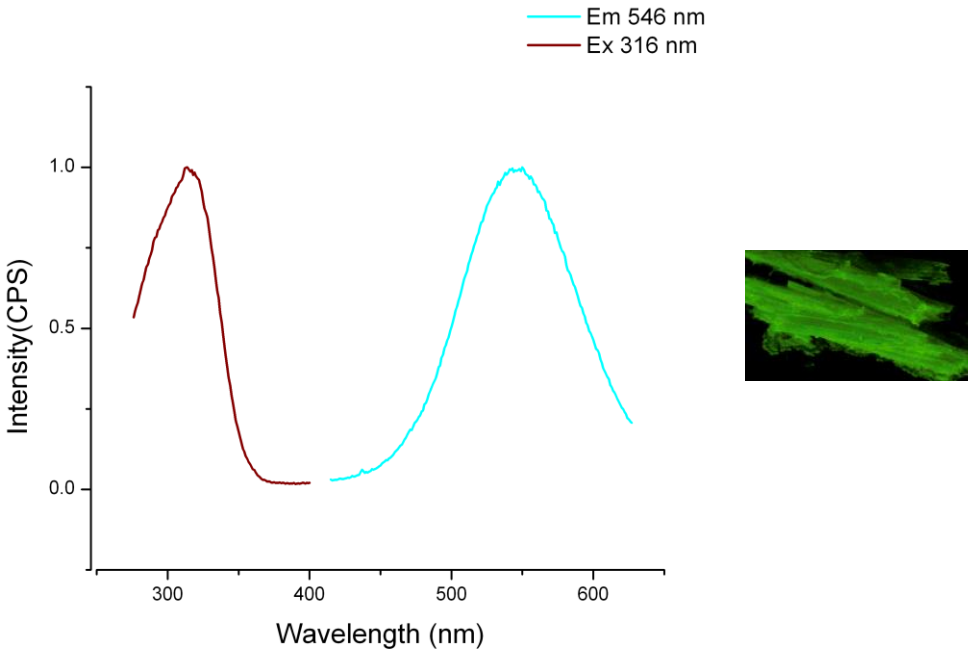

Figure S1. Photoluminescence emission and excitation spectra of **{[Mes][Cu$_3$]}$_\infty$**

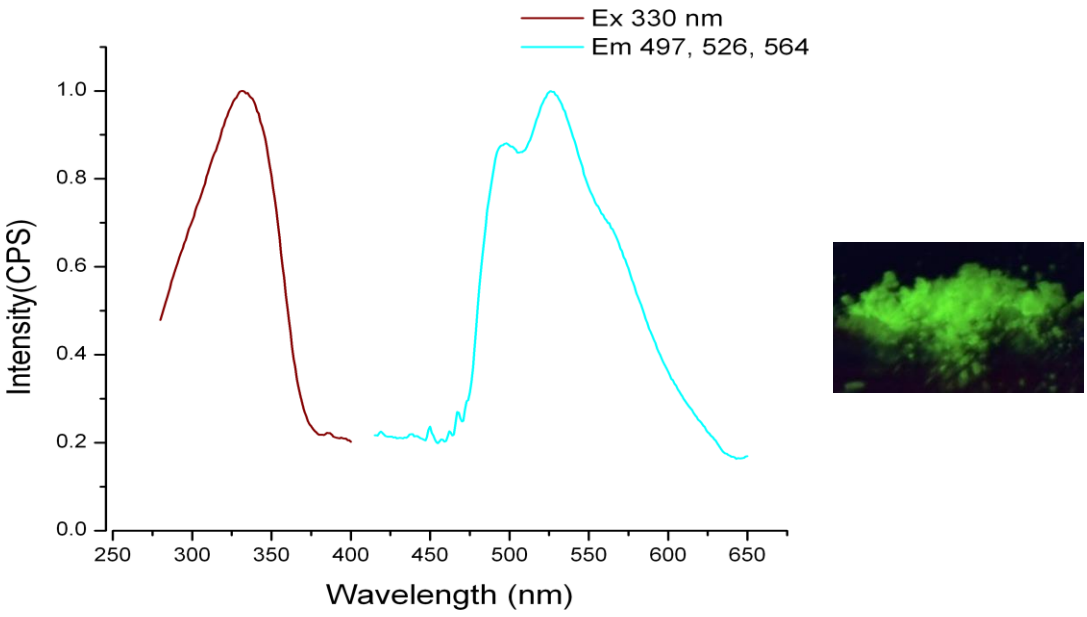

Figure S2. Photoluminescence emission and excitation spectra of **{[Nap][Cu$_3$]}$_\infty$**

X-ray crystallographic data: A suitable crystal covered with a layer of hydrocarbon/paratone-N oil was selected and mounted on a Mitigen loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data were measured on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Crystals of **{[Nap][Cu$_3$]}$_\infty$** appeared to crack at 100 K but diffraction pattern was satisfactory. Data were taken at a slightly higher temperature of 150(2) K for **{[Bz][Cu$_3$]$_2$}$_\infty$** and **{[Mes][Cu$_3$]}$_\infty$** to prevent crystal cracking upon cooling to 100 K. Intensity data were processed using the Saint Plus program. Initial calculations for the structure determination were carried out using the SHELXTL package (version 6.14) and finalized with Olex2 (version 1.2.5). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied by using SADABS. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons.

{[Bz][Cu$_3$]$_2$}$_\infty$ crystallizes in the P-1 space group with one Cu containing molecule and one half molecule of benzene in the asymmetric unit (for a Z value of 2). The center of the benzene molecule is located on an inversion center. Two CF_3 groups demonstrated rotational disorder. It was modeled and the atoms were treated with a combination of SADI, DELU, SIMU, and ISOR restraints as well as occupancy refinements. All the non-hydrogen atoms were refined anisotropically.

{[Mes][Cu$_3$]}$_\infty$ crystallizes in the R3c space group with one-third Cu molecule and one-third molecule of mesitylene in the asymmetric unit (for a Z value of 6). The centers of both molecules

are located at the convergence of three glide planes which effectively creates 3-fold rotational symmetry. All the non-hydrogen atoms were refined anisotropically.

{[Nap][Cu$_3$]}$_\infty$ crystallizes in the P-1 space group with one Cu molecule and two half molecules of naphthalene in the asymmetric unit (for a Z value of 2). The naphthalene molecules are located on an inversion center. One CF_3 group demonstrated rotational disorder and was modeled successfully as well as occupancy refinement. All the non-hydrogen atoms were refined anisotropically.

Additional details are on the CIF files.

Table S1. Crystal data and structure refinement for **{[Bz][Cu$_3$]$_2$}$_\infty$**.

Empirical formula	$C_{36}H_{12}Cu_6F_{36}N_{12}$
Formula weight	1677.82
Temperature/K	150.03
Crystal system	triclinic
Space group	P-1
a/Å	9.560(4)
b/Å	12.620(5)
c/Å	21.550(8)
α/°	88.897(7)
β/°	84.185(7)
γ/°	87.425(7)
Volume/Å^3	2583.8(17)
Z	2
ρ_{calc}g/cm^3	2.157
μ/mm^{-1}	2.600
F(000)	1620.0
Crystal size/mm^3	0.387 × 0.305 × 0.116
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.924 to 53.998
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-27 \le l \le 27$

Reflections collected	28553
Independent reflections	11227 [R_{int} = 0.0250, R_{sigma} = 0.0327]
Data/restraints/parameters	11227/1122/867
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0968
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1056
Largest diff. peak/hole / e $Å^{-3}$	0.99/-0.58

Table S2. Bond Lengths for **{[Bz][Cu$_3$]$_2$}$_\infty$**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu2[1]	3.0309(11)	Cu5	N9	1.867(3)
Cu1	N1	1.872(3)	Cu6	N10	1.871(3)
Cu1	N6	1.870(3)	Cu6	N11	1.868(3)
Cu2	Cu1[1]	3.0310(11)	F19	C19	1.323(5)
Cu2	N2	1.866(3)	F20	C19	1.316(5)
Cu2	N3	1.871(3)	F21	C19	1.322(6)
Cu3	N4	1.871(3)	F22	C20	1.288(5)
Cu3	N5	1.874(3)	F23	C20	1.326(6)
F1	C4	1.336(5)	F24	C20	1.304(6)
F2	C4	1.326(6)	F25	C24	1.335(7)
F3	C4	1.314(5)	F26	C24	1.326(5)
F4	C5	1.332(5)	F27	C24	1.296(5)
F5	C5	1.310(5)	F28	C25	1.279(5)
F6	C5	1.332(5)	F29	C25	1.283(6)
F7	C9	1.445(10)	F30	C25	1.265(6)
F8	C9	1.354(11)	F31	C29	1.339(6)
F9	C9	1.084(10)	F32	C29	1.317(6)
F10	C10	1.266(7)	F33	C29	1.316(5)
F11	C10	1.325(8)	F34	C30	1.345(9)
F12	C10	1.229(8)	F35	C30	1.227(14)
F13	C14	1.320(5)	F36	C30	1.378(13)
F14	C14	1.334(6)	N7	N8	1.363(4)
F15	C14	1.308(5)	N7	C16	1.348(4)
F16	C15	1.304(5)	N8	C18	1.352(4)
F17	C15	1.304(5)	N9	N10	1.355(4)
F18	C15	1.298(5)	N9	C21	1.357(4)
N1	N2	1.363(4)	N10	C23	1.348(4)
N1	C1	1.351(4)	N11	N12	1.368(4)

N2	C3	1.349(4)	N11	C26	1.349(5)
N3	N4	1.365(4)	N12	C28	1.352(5)
N3	C6	1.340(5)	C16	C17	1.375(6)
N4	C8	1.350(5)	C16	C19	1.491(6)
N5	N6	1.358(4)	C17	C18	1.375(6)
N5	C11	1.347(4)	C18	C20	1.488(6)
N6	C13	1.353(4)	C21	C22	1.379(6)
C1	C2	1.382(6)	C21	C24	1.482(6)
C1	C4	1.482(6)	C22	C23	1.370(6)
C2	C3	1.363(6)	C23	C25	1.491(6)
C3	C5	1.495(6)	C26	C27	1.363(6)
C6	C7	1.381(7)	C26	C29	1.498(6)
C6	C9	1.491(6)	C27	C28	1.387(6)
C7	C8	1.383(6)	C28	C30	1.488(6)
C8	C10	1.485(7)	C30	F34A	1.238(14)
C9	F7A	1.166(11)	C30	F35A	1.333(10)
C9	F9A	1.389(9)	C30	F36A	1.368(14)
C9	F8A	1.495(11)	C31	C32	1.390(10)
C11	C12	1.384(6)	C31	C33[2]	1.379(10)
C11	C14	1.485(6)	C32	C33	1.369(9)
C12	C13	1.374(5)	C33	C31[2]	1.378(10)
C13	C15	1.489(6)	C34	C35	1.360(9)
Cu4	N7	1.872(3)	C34	C36[3]	1.371(9)
Cu4	N12	1.868(3)	C35	C36	1.391(9)
Cu5	N8	1.868(3)	C36	C34[3]	1.371(9)

[1]-X,-Y,1-Z; [2]1-X,-Y,1-Z; [3]1-X,1-Y,2-Z

Table S3. Bond Angles for **{[Bz][Cu$_3$]$_2$}$_\infty$**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Cu1	Cu2[1]	100.16(9)	N9	Cu5	N8	172.15(12)
N6	Cu1	Cu2[1]	87.06(8)	N11	Cu6	N10	173.84(12)
N6	Cu1	N1	172.78(12)	N8	N7	Cu4	119.73(19)
N2	Cu2	Cu1[1]	95.88(9)	C16	N7	Cu4	132.0(3)
N2	Cu2	N3	172.16(13)	C16	N7	N8	107.4(3)
N3	Cu2	Cu1[1]	91.92(10)	N7	N8	Cu5	120.36(19)
N4	Cu3	N5	174.24(13)	C18	N8	Cu5	131.7(2)
N2	N1	Cu1	120.0(2)	C18	N8	N7	107.3(3)

C1	N1	Cu1	132.2(3)	N10	N9	Cu5	120.0(2)
C1	N1	N2	107.3(3)	N10	N9	C21	107.2(3)
N1	N2	Cu2	119.6(2)	C21	N9	Cu5	131.9(2)
C3	N2	Cu2	132.7(3)	N9	N10	Cu6	119.64(19)
C3	N2	N1	107.0(3)	C23	N10	Cu6	132.0(3)
N4	N3	Cu2	120.3(2)	C23	N10	N9	107.3(3)
C6	N3	Cu2	131.6(3)	N12	N11	Cu6	120.1(2)
C6	N3	N4	107.2(3)	C26	N11	Cu6	131.1(3)
N3	N4	Cu3	119.7(2)	C26	N11	N12	106.7(3)
C8	N4	Cu3	130.9(3)	N11	N12	Cu4	119.5(2)
C8	N4	N3	107.4(3)	C28	N12	Cu4	132.3(3)
N6	N5	Cu3	119.42(19)	C28	N12	N11	107.4(3)
C11	N5	Cu3	131.4(3)	N7	C16	C17	110.7(3)
C11	N5	N6	107.6(3)	N7	C16	C19	121.0(4)
N5	N6	Cu1	120.54(19)	C17	C16	C19	128.1(3)
C13	N6	Cu1	131.3(2)	C16	C17	C18	104.1(3)
C13	N6	N5	107.5(3)	N8	C18	C17	110.5(3)
N1	C1	C2	110.5(4)	N8	C18	C20	121.0(3)
N1	C1	C4	121.1(3)	C17	C18	C20	128.3(3)
C2	C1	C4	128.2(4)	F19	C19	C16	113.4(3)
C3	C2	C1	103.7(3)	F20	C19	F19	107.4(4)
N2	C3	C2	111.5(3)	F20	C19	F21	107.3(4)
N2	C3	C5	120.6(4)	F20	C19	C16	111.2(4)
C2	C3	C5	127.9(4)	F21	C19	F19	105.0(4)
F1	C4	C1	112.2(4)	F21	C19	C16	112.1(3)
F2	C4	F1	103.6(4)	F22	C20	F23	106.6(5)
F2	C4	C1	113.6(4)	F22	C20	F24	108.9(5)
F3	C4	F1	107.8(4)	F22	C20	C18	111.8(4)
F3	C4	F2	106.5(5)	F23	C20	C18	111.0(4)
F3	C4	C1	112.5(4)	F24	C20	F23	104.4(4)
F4	C5	F6	106.8(4)	F24	C20	C18	113.7(4)
F4	C5	C3	111.0(4)	N9	C21	C22	110.7(3)
F5	C5	F4	107.6(4)	N9	C21	C24	120.9(3)
F5	C5	F6	106.3(4)	C22	C21	C24	128.4(3)
F5	C5	C3	113.3(3)	C23	C22	C21	103.4(3)
F6	C5	C3	111.5(4)	N10	C23	C22	111.4(3)
N3	C6	C7	111.4(4)	N10	C23	C25	120.5(4)
N3	C6	C9	121.8(4)	C22	C23	C25	128.1(3)

C7	C6	C9	126.5(4)	F25	C24	C21	113.1(4)
C6	C7	C8	103.2(4)	F26	C24	F25	102.4(4)
N4	C8	C7	110.7(4)	F26	C24	C21	112.6(4)
N4	C8	C10	121.9(4)	F27	C24	F25	106.6(5)
C7	C8	C10	127.4(4)	F27	C24	F26	108.2(4)
F7	C9	C6	105.3(6)	F27	C24	C21	113.1(4)
F8	C9	F7	98.2(8)	F28	C25	F29	104.9(5)
F8	C9	C6	109.4(5)	F28	C25	C23	113.0(4)
F9	C9	F7	112.3(10)	F29	C25	C23	112.3(4)
F9	C9	F8	114.1(11)	F30	C25	F28	109.4(5)
F9	C9	C6	115.8(7)	F30	C25	F29	102.7(6)
C6	C9	F8A	110.9(5)	F30	C25	C23	113.6(4)
F7A	C9	C6	120.4(8)	N11	C26	C27	112.0(4)
F7A	C9	F9A	110.1(10)	N11	C26	C29	119.8(4)
F7A	C9	F8A	106.9(12)	C27	C26	C29	128.3(4)
F9A	C9	C6	113.3(6)	C26	C27	C28	103.4(4)
F9A	C9	F8A	91.2(7)	N12	C28	C27	110.6(4)
F10	C10	F11	101.1(6)	N12	C28	C30	121.5(4)
F10	C10	C8	114.7(5)	C27	C28	C30	127.7(4)
F11	C10	C8	111.4(5)	F31	C29	C26	111.6(4)
F12	C10	F10	112.0(6)	F32	C29	F31	105.9(5)
F12	C10	F11	101.9(6)	F32	C29	C26	113.5(4)
F12	C10	C8	114.1(6)	F33	C29	F31	105.7(4)
N5	C11	C12	110.5(3)	F33	C29	F32	107.9(5)
N5	C11	C14	121.4(3)	F33	C29	C26	111.8(4)
C12	C11	C14	128.1(3)	F34	C30	F36	100.5(8)
C13	C12	C11	103.9(3)	F34	C30	C28	112.4(6)
N6	C13	C12	110.5(3)	F35	C30	F34	110.6(8)
N6	C13	C15	120.7(3)	F35	C30	F36	103.0(11)
C12	C13	C15	128.7(3)	F35	C30	C28	116.4(8)
F13	C14	F14	104.9(5)	F36	C30	C28	112.4(6)
F13	C14	C11	112.2(4)	F34A	C30	C28	111.8(8)
F14	C14	C11	112.8(4)	F34A	C30	F35A	113.1(9)
F15	C14	F13	108.0(4)	F34A	C30	F36A	110.7(13)
F15	C14	F14	107.1(5)	F35A	C30	C28	110.5(7)
F15	C14	C11	111.4(4)	F35A	C30	F36A	99.9(9)
F16	C15	C13	112.5(3)	F36A	C30	C28	110.1(6)
F17	C15	F16	107.0(4)	C33[2]	C31	C32	120.0(7)

F17	C15	C13	112.1(4)	C33	C32	C31	119.3(7)
F18	C15	F16	104.4(4)	C32	C33	C31[2]	120.7(7)
F18	C15	F17	107.1(4)	C35	C34	C36[3]	121.1(6)
F18	C15	C13	113.2(3)	C34	C35	C36	119.2(6)
N12	Cu4	N7	173.12(12)	C34[3]	C36	C35	119.7(6)

[1]-X,-Y,1-Z; [2]1-X,-Y,1-Z; [3]1-X,1-Y,2-Z

Table S4. Atomic Occupancy for **{[Bz][Cu$_3$]$_2$}$_\infty$**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F7	0.487(6)	F8	0.513(6)	F9	0.487(6)
F34	0.50(2)	F35	0.50(2)	F36	0.50(2)
F7A	0.513(6)	F9A	0.513(6)	F8A	0.487(6)
F34A	0.50(2)	F35A	0.50(2)	F36A	0.50(2)

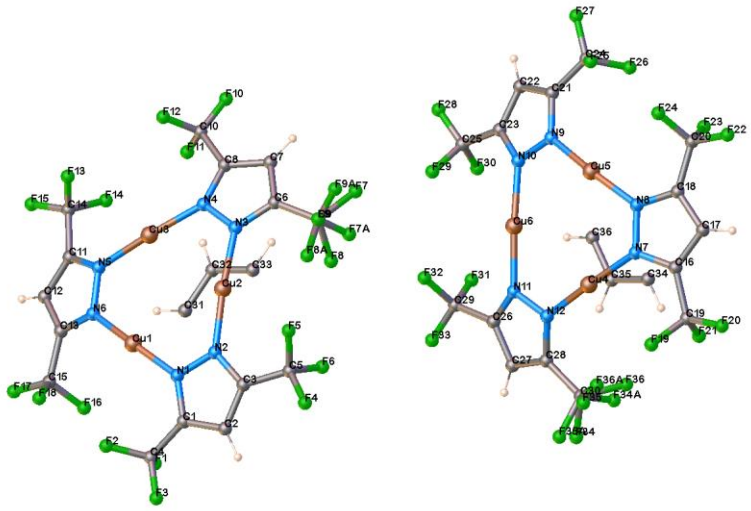

Figure S3. View of asymmetric unit and atom labeling of **{[Bz][Cu$_3$]$_2$}$_\infty$**

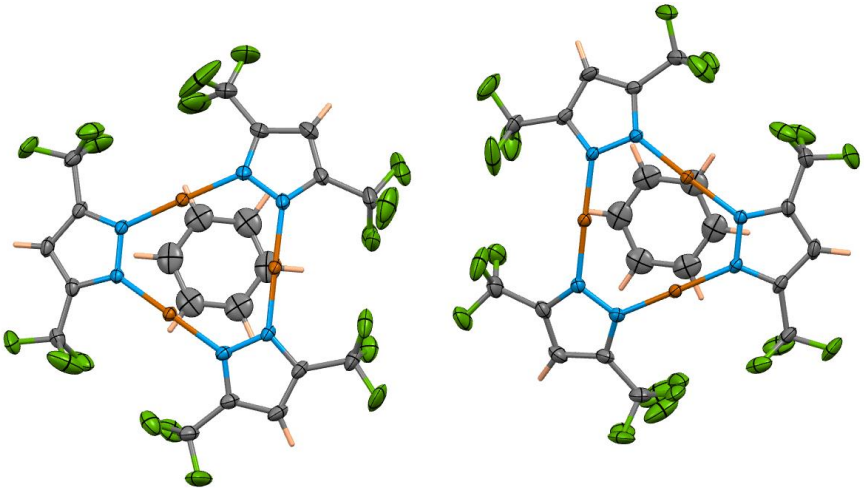

Figure S4. View of $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and benzene in **{[Bz][Cu$_3$]$_2$}$_\infty$**

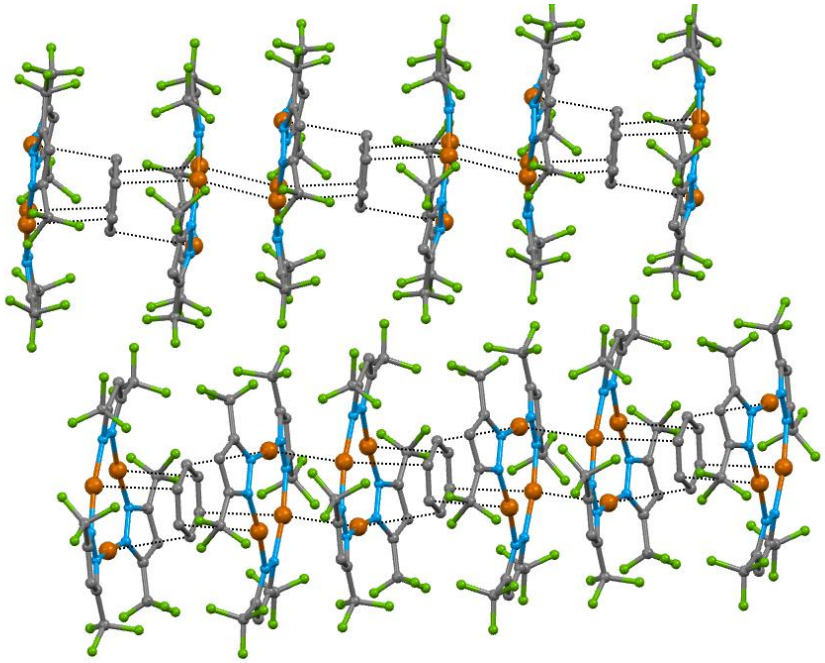

Figure S5. View of columnar structure and Cu···Cu interactions of **{[Bz][Cu$_3$]$_2$}$_\infty$**

Table S5. Crystal data and structure refinement for **{[Mes][Cu$_3$]}$_\infty$** .

Empirical formula	$C_{24}H_{15}Cu_3F_{18}N_6$
Formula weight	920.04
Temperature/K	150.0
Crystal system	trigonal
Space group	R3c
a/Å	19.975(2)
b/Å	19.975(2)
c/Å	13.2744(14)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	4586.8(11)
Z	6
ρ_{calc}g/cm^3	1.998
μ/mm^{-1}	2.207
F(000)	2700.0
Crystal size/mm^3	0.41 × 0.31 × 0.26
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.948 to 80.536
Index ranges	$-35 \le h \le 35$, $-35 \le k \le 35$, $-23 \le l \le 23$
Reflections collected	36711
Independent reflections	6277 [R_{int} = 0.0274, R_{sigma} = 0.0311]
Data/restraints/parameters	6277/1/155
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0634
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.0659
Largest diff. peak/hole / e Å^{-3}	0.45/-0.42

Table S6. Bond Lengths for **{[Mes][Cu$_3$]}$_\infty$** .

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cu	N1	1.8689(13)	N2	Cu^2	1.8720(13)
Cu	N2^1	1.8720(13)	N2	C3	1.346(2)
F1	C4	1.322(3)	C1	C2	1.387(2)
F2	C4	1.315(2)	C1	C4	1.489(2)
F3	C4	1.335(3)	C2	C3	1.383(2)

F4	C5	1.317(2)	C3	C5	1.494(2)
F5	C5	1.321(3)	C6	C7[1]	1.392(3)
F6	C5	1.324(3)	C6	C7	1.396(3)
N1	N2	1.3554(19)	C6	C8	1.510(3)
N1	C1	1.347(2)	C7	C6[2]	1.392(3)

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z

Table S7. Bond Angles for **{[Mes][Cu_3]}$_\infty$**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Cu	N2[1]	178.25(6)	F1	C4	C1	112.49(17)
N2	N1	Cu	117.73(10)	F2	C4	F1	108.2(2)
C1	N1	Cu	133.18(12)	F2	C4	F3	106.8(2)
C1	N1	N2	107.48(13)	F2	C4	C1	111.61(16)
N1	N2	Cu[2]	118.24(10)	F3	C4	C1	112.51(18)
C3	N2	Cu[2]	132.77(11)	F4	C5	F5	107.7(2)
C3	N2	N1	107.75(13)	F4	C5	F6	106.7(2)
N1	C1	C2	110.80(14)	F4	C5	C3	111.46(16)
N1	C1	C4	120.86(15)	F5	C5	F6	106.2(2)
C2	C1	C4	128.27(15)	F5	C5	C3	112.00(16)
C3	C2	C1	103.17(13)	F6	C5	C3	112.45(17)
N2	C3	C2	110.79(14)	C7[1]	C6	C7	118.64(18)
N2	C3	C5	120.68(14)	C7[1]	C6	C8	120.6(2)
C2	C3	C5	128.48(15)	C7	C6	C8	120.71(19)
F1	C4	F3	104.9(2)	C6[2]	C7	C6	121.36(18)

[1]1-Y,1+X-Y,+Z; [2]+Y-X,1-X,+Z

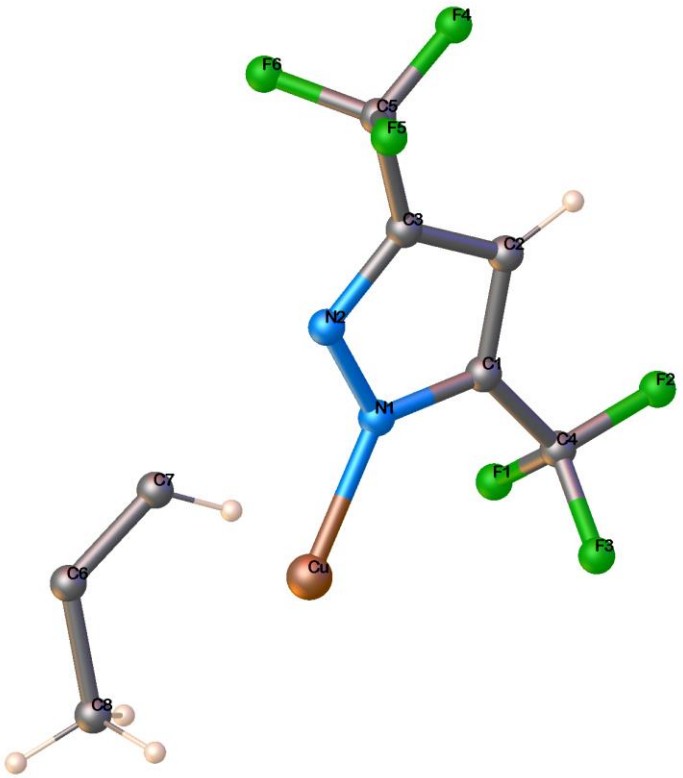

Figure S6. View of asymmetric unit and atom labeling of **{[Mes][Cu$_3$]}$_\infty$**

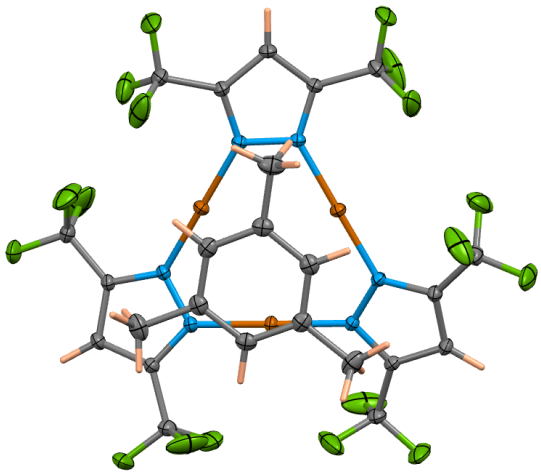

Figure S7. View of {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ and mesitylene in **{[Mes][Cu$_3$]}$_\infty$**

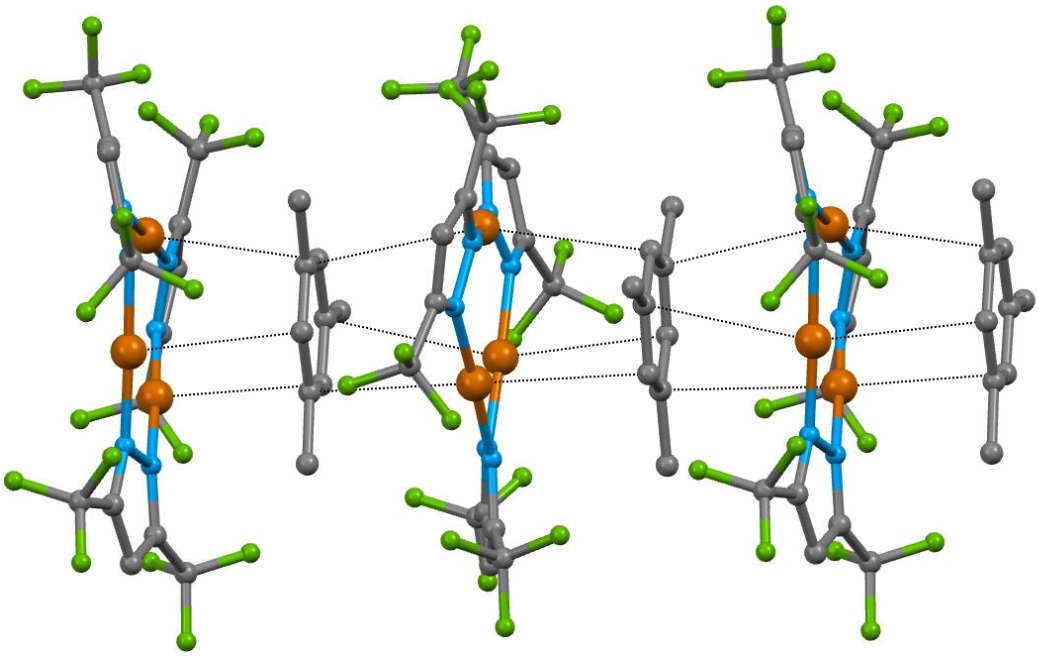

Figure S8. View of columnar structure of **{[Mes][Cu$_3$]}$_\infty$**

Table S8. Crystal data and structure refinement for **{[Nap][Cu_3]}$_\infty$** .

Identification code	rad194_0m_a_final
Empirical formula	$C_{25}H_{11}Cu_3F_{18}N_6$
Formula weight	928.02
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.7936(11)
b/Å	12.4534(11)
c/Å	12.7263(11)
α/°	109.803(2)
β/°	117.447(2)
γ/°	95.807(2)
Volume/Å^3	1484.7(2)
Z	2
ρ_{calc}g/cm^3	2.076
μ/mm^{-1}	2.274
F(000)	904.0
Crystal size/mm^3	0.505 × 0.292 × 0.146
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.27 to 54
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	16256
Independent reflections	6379 [R_{int} = 0.0134, R_{sigma} = 0.0159]
Data/restraints/parameters	6379/61/500
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0223, wR_2 = 0.0569
Final R indexes [all data]	R_1 = 0.0235, wR_2 = 0.0576
Largest diff. peak/hole / e Å^{-3}	0.43/-0.36

Table S9. Bond Lengths for **{[Nap][Cu_3]}$_\infty$** .

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N1	1.8720(13)	C2	C3	1.383(2)
Cu1	N6	1.8719(13)	C3	C5	1.493(2)
Cu2	N2	1.8671(13)	C6	C7	1.381(2)

Cu2	N3	1.8738(13)	C6	C9	1.502(3)
Cu3	N4	1.8770(13)	C6	C9A	1.491(7)
Cu3	N5	1.8757(13)	C7	C8	1.384(2)
F1	C4	1.3358(18)	C8	C10	1.495(2)
F2	C4	1.3441(19)	C9	F7	1.340(3)
F3	C4	1.3476(19)	C9	F8	1.329(3)
F4	C5	1.3355(19)	C9	F9	1.338(3)
F5	C5	1.3440(19)	C9A	F8A	1.329(5)
F6	C5	1.3351(19)	C9A	F7A	1.334(5)
F10	C10	1.334(2)	C9A	F9A	1.329(5)
F11	C10	1.329(2)	C11	C12	1.385(2)
F12	C10	1.331(2)	C11	C14	1.491(2)
F13	C14	1.337(2)	C12	C13	1.384(2)
F14	C14	1.335(2)	C13	C15	1.493(2)
F15	C14	1.3292(19)	C16	C17	1.371(3)
F16	C15	1.3365(19)	C16	C20[1]	1.412(3)
F17	C15	1.341(2)	C17	C18	1.414(3)
F18	C15	1.3346(19)	C18	C19	1.372(3)
N1	N2	1.3619(17)	C19	C20	1.413(3)
N1	C1	1.3451(19)	C20	C16[1]	1.412(3)
N2	C3	1.3495(19)	C20	C20[1]	1.438(3)
N3	N4	1.3617(18)	C21	C22	1.373(3)
N3	C6	1.3493(19)	C21	C25[2]	1.420(3)
N4	C8	1.3442(19)	C22	C23	1.406(3)
N5	N6	1.3570(17)	C23	C24	1.373(3)
N5	C11	1.3462(19)	C24	C25	1.419(3)
N6	C13	1.3457(19)	C25	C21[2]	1.420(3)
C1	C2	1.385(2)	C25	C25[2]	1.422(4)
C1	C4	1.492(2)			

[1]1-X,-Y,1-Z; [2]1-X,1-Y,2-Z

Table S10 Bond Angles for **{[Nap][Cu_3]}$_\infty$** .

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N6	Cu1	N1	178.26(5)	F8	C9	C6	110.6(2)
N2	Cu2	N3	173.08(6)	F8	C9	F7	107.1(3)
N5	Cu3	N4	173.75(6)	F8	C9	F9	106.4(2)
N2	N1	Cu1	119.00(10)	F9	C9	C6	113.7(2)

C1	N1	Cu1	133.09(10)	F9	C9	F7	106.6(2)
C1	N1	N2	107.38(12)	F8A	C9A	C6	116.2(6)
N1	N2	Cu2	119.60(10)	F8A	C9A	F7A	108.0(6)
C3	N2	Cu2	132.75(11)	F8A	C9A	F9A	106.9(6)
C3	N2	N1	107.43(12)	F7A	C9A	C6	111.1(9)
N4	N3	Cu2	118.17(10)	F9A	C9A	C6	108.0(5)
C6	N3	Cu2	132.63(11)	F9A	C9A	F7A	106.1(6)
C6	N3	N4	107.41(12)	F10	C10	C8	112.56(15)
N3	N4	Cu3	118.29(10)	F11	C10	F10	105.77(14)
C8	N4	Cu3	133.46(11)	F11	C10	F12	107.42(16)
C8	N4	N3	107.47(12)	F11	C10	C8	110.95(14)
N6	N5	Cu3	119.66(10)	F12	C10	F10	107.22(16)
C11	N5	Cu3	132.70(11)	F12	C10	C8	112.54(14)
C11	N5	N6	107.63(12)	N5	C11	C12	110.84(13)
N5	N6	Cu1	119.86(9)	N5	C11	C14	120.80(13)
C13	N6	Cu1	132.68(11)	C12	C11	C14	128.35(14)
C13	N6	N5	107.45(12)	C13	C12	C11	103.07(13)
N1	C1	C2	111.16(13)	N6	C13	C12	111.01(13)
N1	C1	C4	120.15(14)	N6	C13	C15	121.44(14)
C2	C1	C4	128.69(14)	C12	C13	C15	127.44(14)
C3	C2	C1	103.08(13)	F13	C14	C11	112.47(13)
N2	C3	C2	110.95(13)	F14	C14	F13	105.97(14)
N2	C3	C5	120.73(13)	F14	C14	C11	112.58(14)
C2	C3	C5	128.30(14)	F15	C14	F13	106.72(15)
F1	C4	F2	107.69(13)	F15	C14	F14	107.07(14)
F1	C4	F3	107.07(12)	F15	C14	C11	111.61(13)
F1	C4	C1	110.96(13)	F16	C15	F17	105.81(13)
F2	C4	F3	105.89(13)	F16	C15	C13	112.98(13)
F2	C4	C1	112.62(13)	F17	C15	C13	112.07(13)
F3	C4	C1	112.28(13)	F18	C15	F16	107.67(13)
F4	C5	F5	107.14(13)	F18	C15	F17	106.87(13)
F4	C5	C3	111.02(13)	F18	C15	C13	111.07(13)
F5	C5	C3	111.75(13)	C17	C16	$C20^{1}$	121.41(17)
F6	C5	F4	107.07(13)	C16	C17	C18	120.04(17)
F6	C5	F5	106.29(13)	C19	C18	C17	119.95(17)
F6	C5	C3	113.22(13)	C18	C19	C20	121.59(17)
N3	C6	C7	110.85(14)	$C16^{1}$	C20	C19	122.99(16)
N3	C6	C9	120.45(16)	$C16^{1}$	C20	$C20^{1}$	118.7(2)

N3	C6	C9A	123.1(3)	C19	C20	C20[1]	118.3(2)
C7	C6	C9	128.53(16)	C22	C21	C25[2]	120.47(19)
C7	C6	C9A	124.8(3)	C21	C22	C23	120.54(18)
C6	C7	C8	103.30(13)	C24	C23	C22	120.31(19)
N4	C8	C7	110.96(14)	C23	C24	C25	120.8(2)
N4	C8	C10	121.92(14)	C21[2]	C25	C25[2]	119.1(2)
C7	C8	C10	127.11(14)	C24	C25	C21[2]	122.09(19)
F7	C9	C6	112.0(3)	C24	C25	C25[2]	118.8(2)

[1]1-X,-Y,1-Z; [2]1-X,1-Y,2-Z

Table S11 Atomic Occupancy for **{[Nap][Cu$_3$]}$_\infty$** .

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C9	0.762(4)	F7	0.762(4)	F8	0.762(4)
F9	0.762(4)	C9A	0.238(4)	F8A	0.238(4)
F7A	0.238(4)	F9A	0.238(4)		

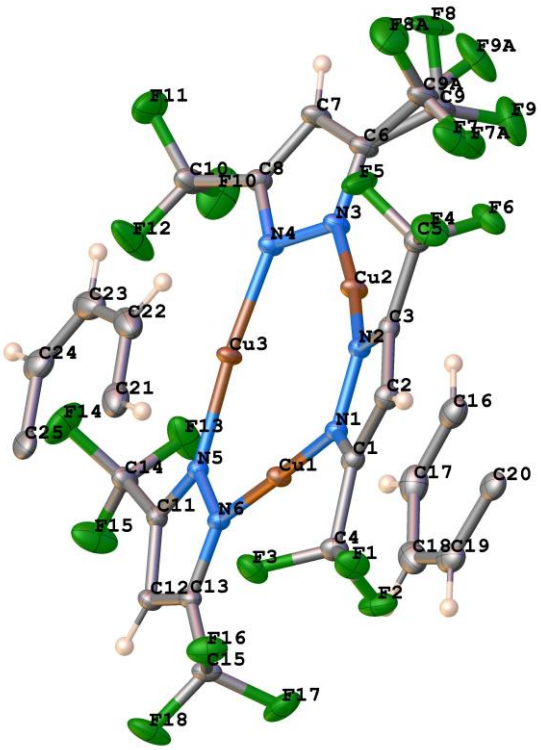

Figure S9. View of asymmetric unit and atom labeling of **{[Nap][Cu$_3$]}$_\infty$**

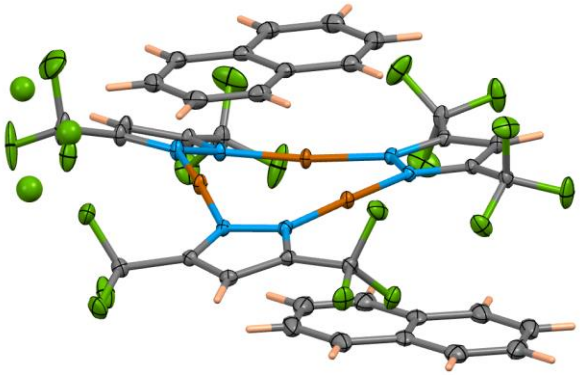

Figure S10. View of {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ and naphthalene in **{[Nap][Cu$_3$]}$_\infty$**

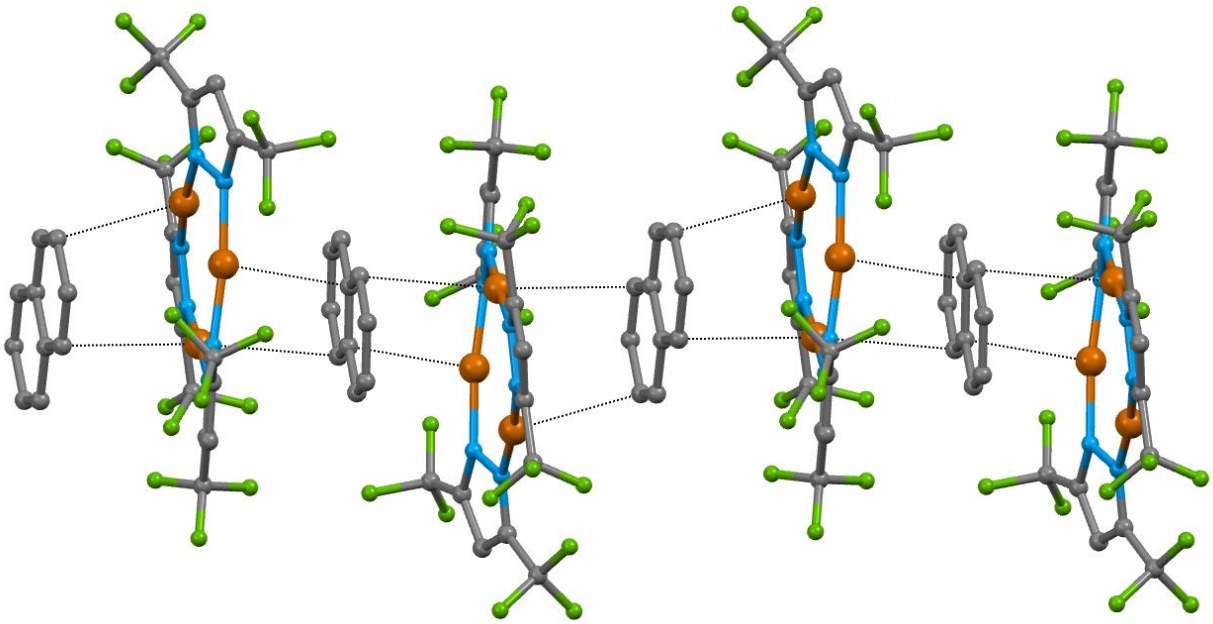

Figure S11. View of columnar structure of **{[Nap][Cu$_3$]}$_\infty$**