

Supporting Information

CFA-13 - a bifunctional perfluorinated metal-organic framework featuring active Cu(I) and Cu(II) sites

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1. Gas sorption measurements

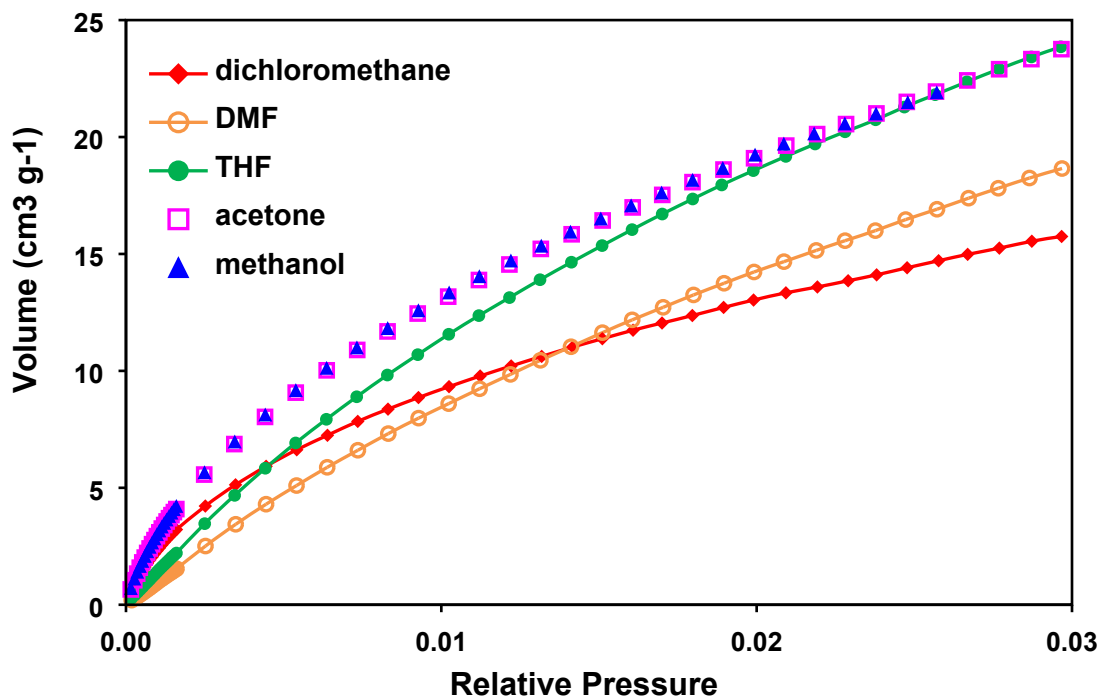


Fig. S1 CO₂ adsorption isotherms at 273 K for as-synthesized (Me₂NH₂)[CFA-13](DMF) and solvent-exchanged samples.

The isosteric heats of adsorption were calculated from the measured isotherms (Figs. S2-3) using the Clausius-Clapeyron equation (I). The slopes of linear plots $\ln P$ versus $1/RT$ for different loadings (Fig. S4-5) give the adsorption enthalpies, according to the equation (II).

$$Q_{st} = -R \left(\frac{\partial(\ln P)}{\partial(1/T)} \right)_{\theta} \quad (\text{I}), \theta - \text{surface coverage}$$

$$\ln P = -\frac{Q_{st}}{R} \left(\frac{1}{T} \right) + C \quad (\text{II}), C - \text{integration constant}$$

The isosteric heat of O₂ adsorption at zero limit surface coverage (initial heat of adsorption) has been determined using Henry's constants K_H , obtained as a slope from the linear ranges of isotherms at low pressure (Table S1 and Fig. S6). In this range the dependence of amount adsorbed (n) on pressure can be expressed with Henry's law (III). The initial isosteric heat of adsorption is obtained similarly using the Clausius-Clapeyron equation (IV) (Fig. S7).

$$n = K_H \cdot P \quad (\text{III})$$

$$\lim_{n \rightarrow 0} (Q_{st}) = Q_{st}^0 = R \left(\frac{\partial (\ln K_H)}{\partial (1/T)} \right) \quad (\text{IV})$$

Table S1. Henry's constants for O₂ adsorption on (Me₂NH₂)[CFA-13](THF) (cm³ g⁻¹ kPa⁻¹)

T [K]	163	173	183
K _H	4.45	2.25	1.20

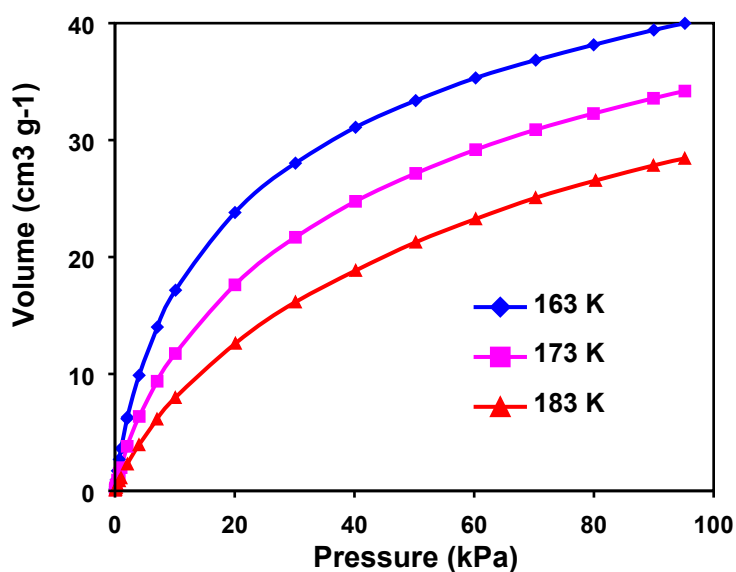


Fig. S2 O₂ adsorption isotherms for (Me₂NH₂)[CFA-13](THF) at different temperatures.

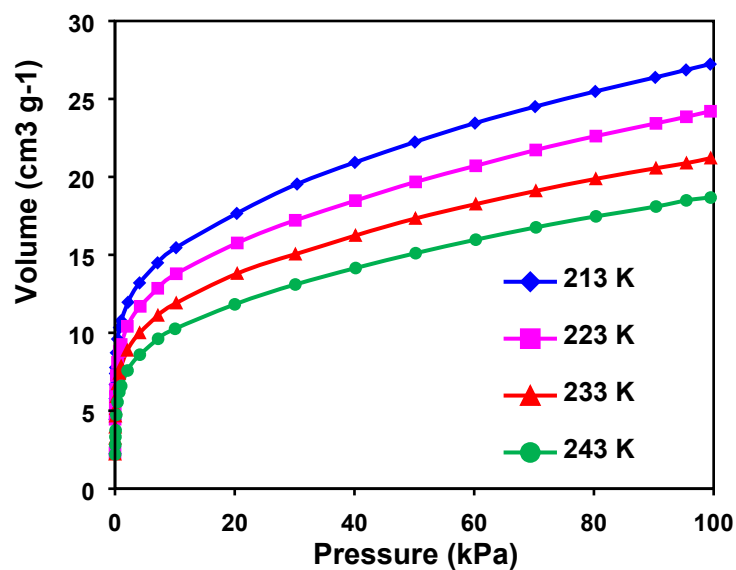


Fig. S3 CO adsorption isotherms for (Me₂NH₂)[CFA-13](THF) at different temperatures.

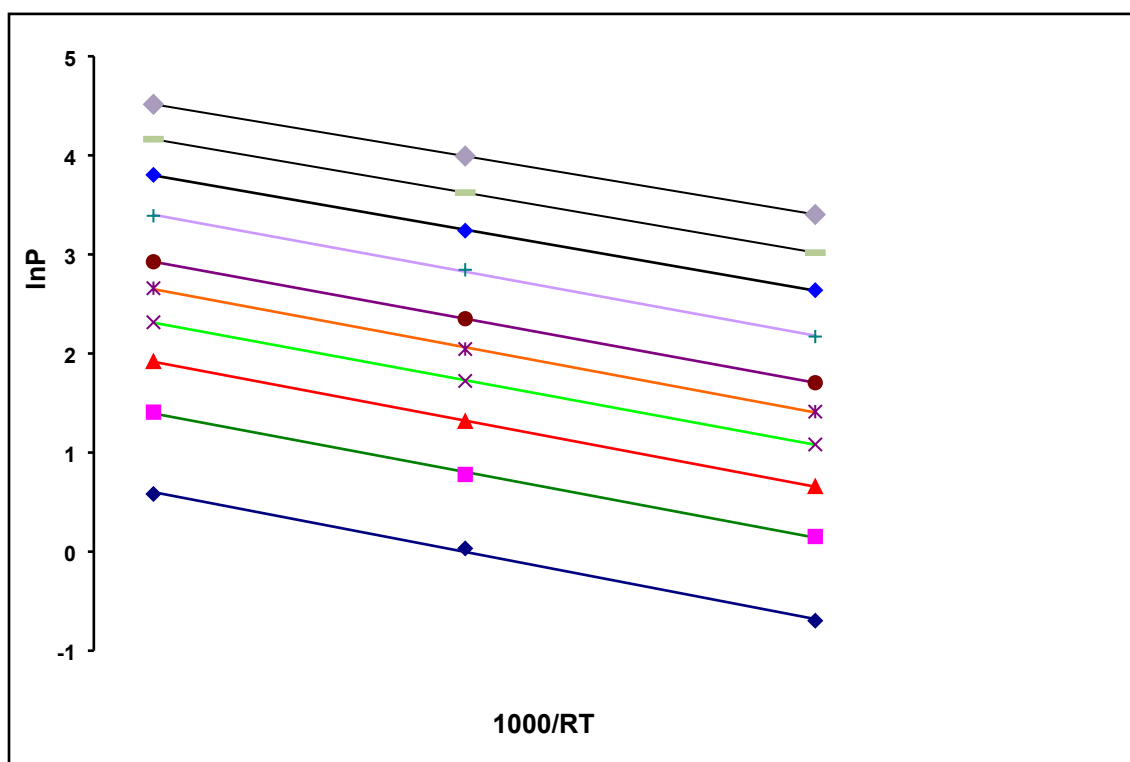


Fig. S4 $\ln P$ versus $1/RT$ plots for different loadings for O_2 adsorption on $(Me_2NH_2)[CFA-13](THF)$.

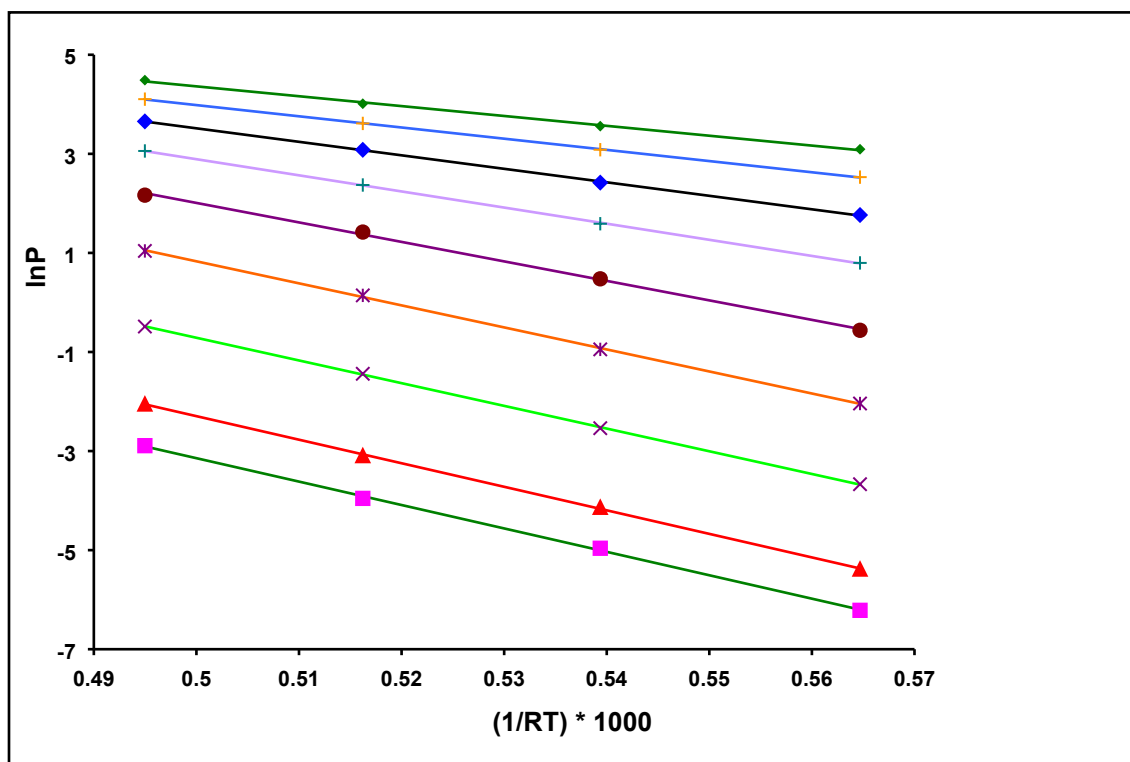


Fig. S5 $\ln P$ versus $1/RT$ plots for different loadings for CO adsorption on $(Me_2NH_2)[CFA-13](THF)$.

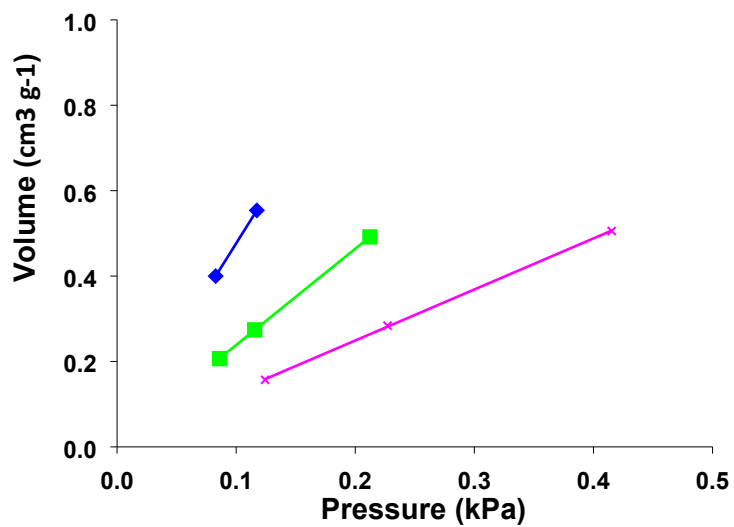


Fig. S6 Determination of Henry's constants for O₂ adsorption on (Me₂NH₂)[CFA-13](THF).

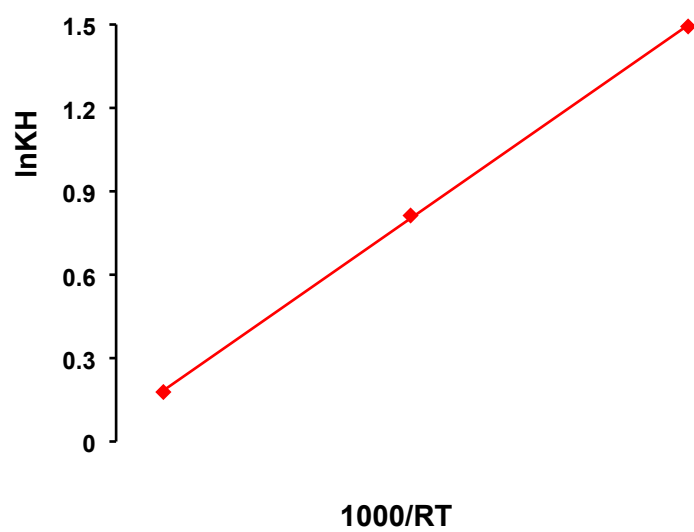


Fig. S7 $\ln K_H$ versus $1/RT$ plot for O₂ adsorption on (Me₂NH₂)[CFA-13](THF).

2. TGA measurements

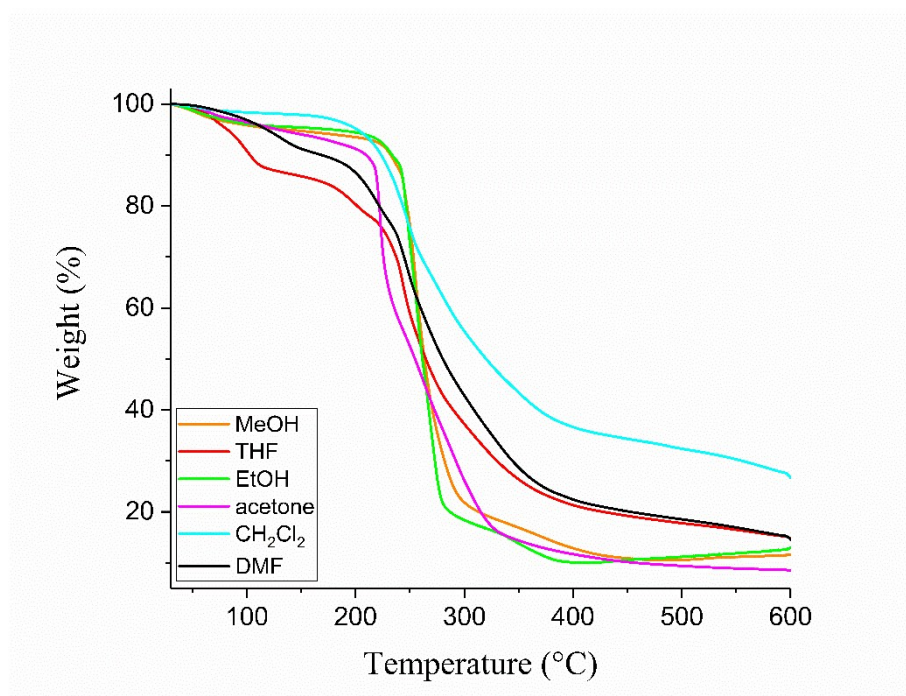


Fig. S8 Temperature dependent weight loss of $(\text{Me}_2\text{NH}_2)[\text{CFA-13}]$ filled with different solvents under flowing nitrogen gas up to 600 °C.

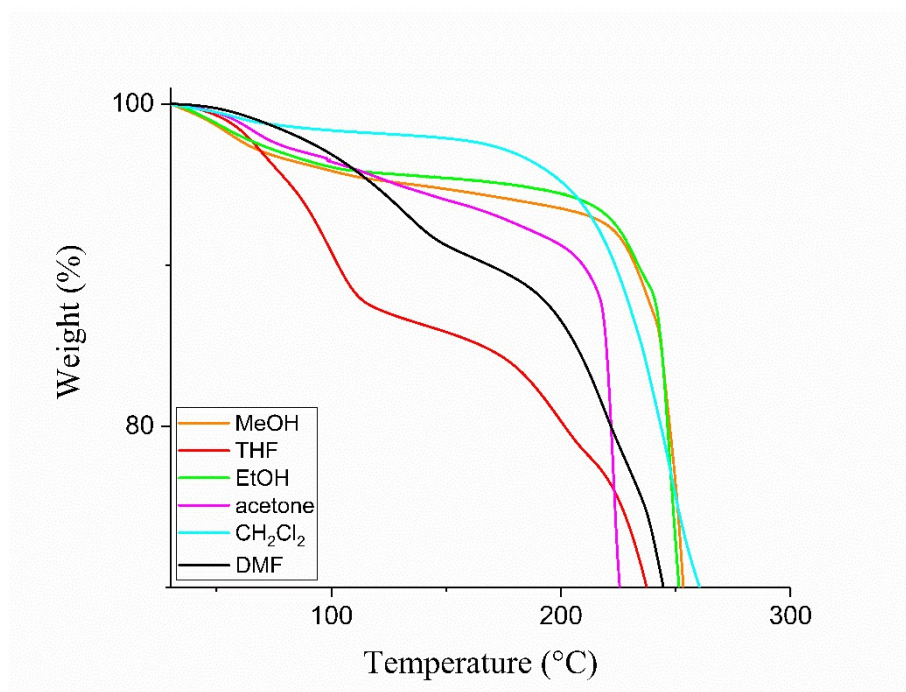


Fig. S9 Temperature dependent weight loss of $(\text{Me}_2\text{NH}_2)[\text{CFA-13}]$ filled with different solvents under flowing nitrogen gas from room temperature to 300 °C.

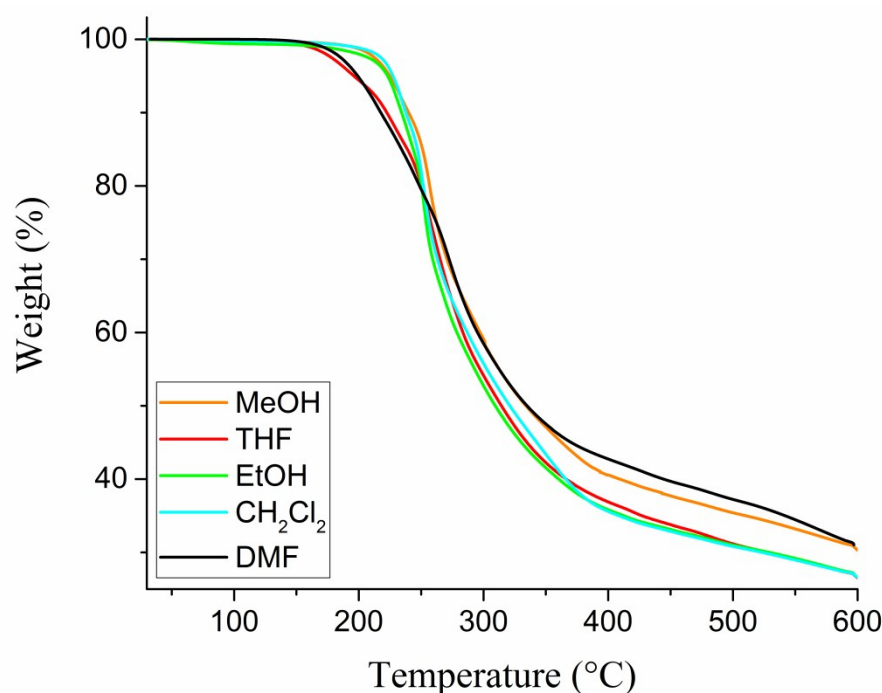


Fig. S10 Temperature dependent weight loss of $(\text{Me}_2\text{NH}_2)[\text{CFA-13}]$ under flowing nitrogen gas after activation of 150 °C.

$(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{THF})$ (red line) shows similar behaviour as $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{DMF})$ but with a larger first weight loss step at lower temperature and a smaller step at higher temperature. This leads to the fact that the sample has lower fraction of high boiling point solvent as compared to $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{DMF})$. Nevertheless, the similar curve progression gives the first evidence that the exchange of DMF by THF was not complete. $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{MeOH})$, shows a stable plateau in the range 100-200 °C, whereas $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{EtOH})$ and $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{CH}_2\text{Cl}_2)$ are stable up to approx. 170 °C (Figs. S8 and S9). No stable plateau is observed for $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{DMF})$ and $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{acetone})$ samples. In order to prove the efficiency of the solvent exchange with MeOH, THF, EtOH, and CH_2Cl_2 , the samples were degassed at 150 °C under nitrogen flow until constant weight and examined by TGA again afterwards. $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{MeOH})$, $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{EtOH})$ and $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{CH}_2\text{Cl}_2)$ show stable plateaus up to 200 °C now (Fig. S10), which demonstrates that residual and coordinated solvent molecules were successfully removed. The TGA curve of the pre-heated $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{THF})$ sample is similar to $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{DMF})$, showing that the exchange of DMF molecules by THF was not complete.

Furthermore, the solvent exchange was monitored by IR-spectroscopy. The solvent is fully exchanged in by acetone, CH_2Cl_2 and MeOH (Figs. S11 and S12), whereas $(\text{Me}_2\text{NH}_2)[\text{CFA-13}](\text{THF})$ still contains a small DMF residue, as can be seen by the characteristic band at 1666 cm^{-1} (Fig. S12).

3. IR spectra

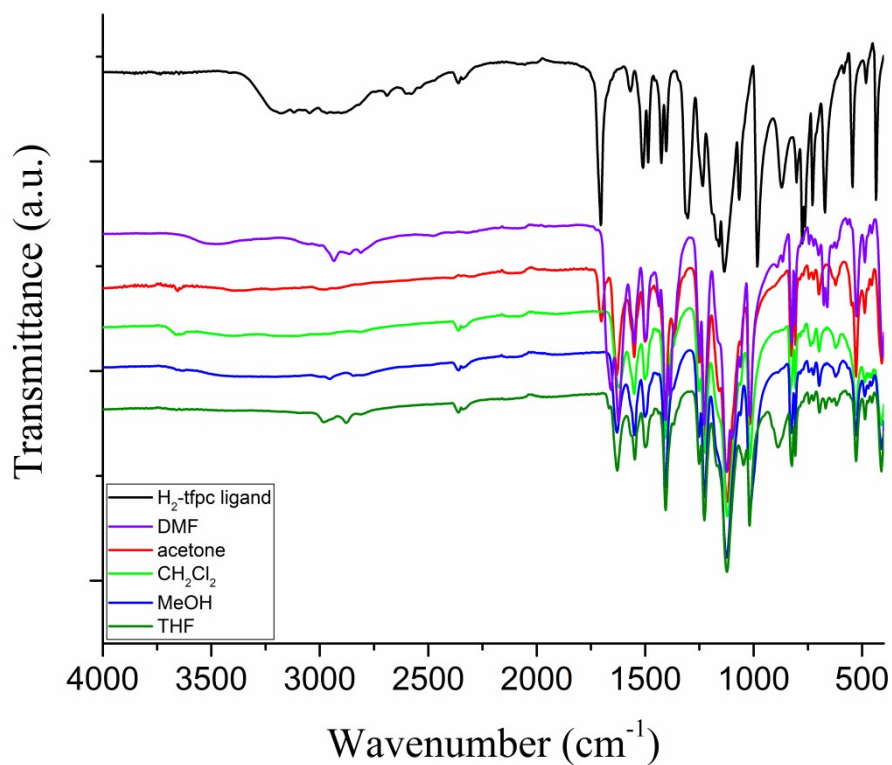


Fig. S11 IR spectra of the H_2 -tfpc ligand and various $(Me_2NH_2)[CFA-13](\text{solvent})$ samples.

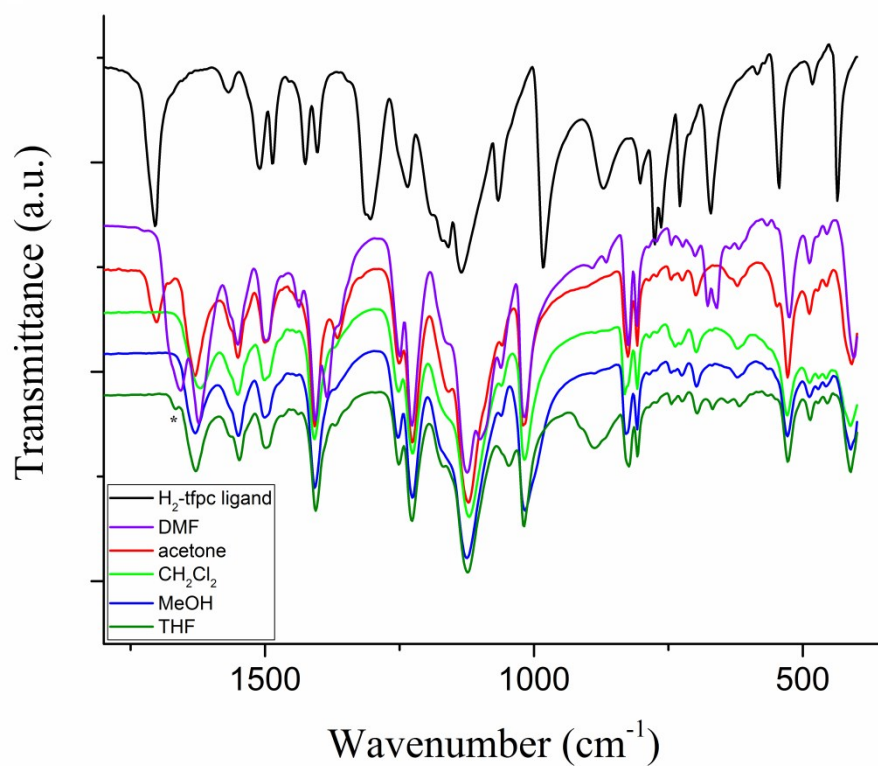


Fig. S12 IR spectra in the range 1800-400 cm^{-1} of the H_2 -tfpc ligand and various $(Me_2NH_2)[CFA-13](\text{solvent})$ samples (* - a characteristic band of coordinated DMF molecules).

4. Ammonia Pulse Chemisorption Measurement

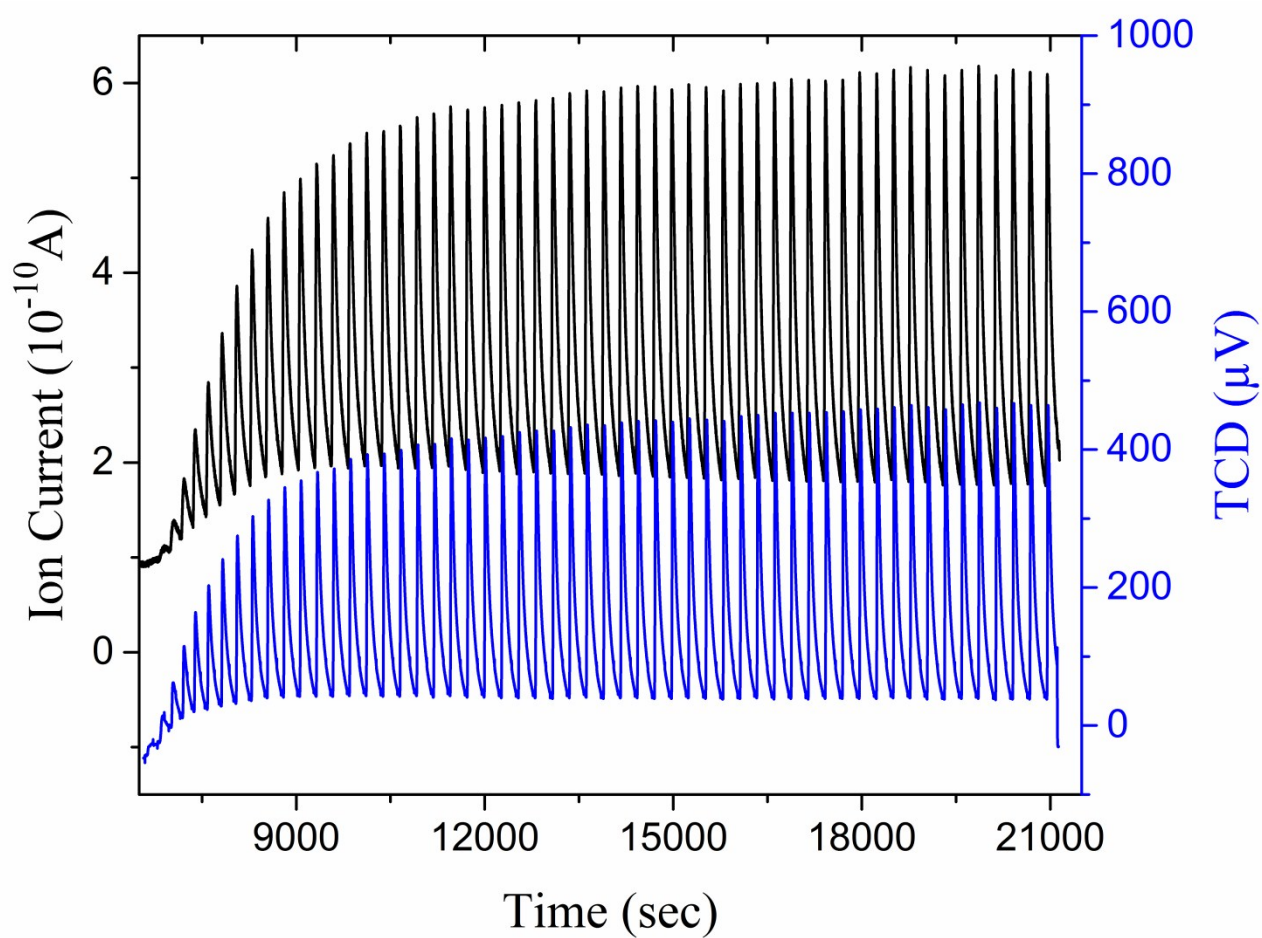


Fig. S13 Ammonia pulse chemisorption at $(\text{Me}_2\text{NH}_2)[\text{CFA-13}]$. Measurement of 56 pulses, 55 pulses were used for further analysis. Blue curve: TCD signal; Black curve: mass spectrum m/z 17.

5. X-Ray powder diffraction patterns

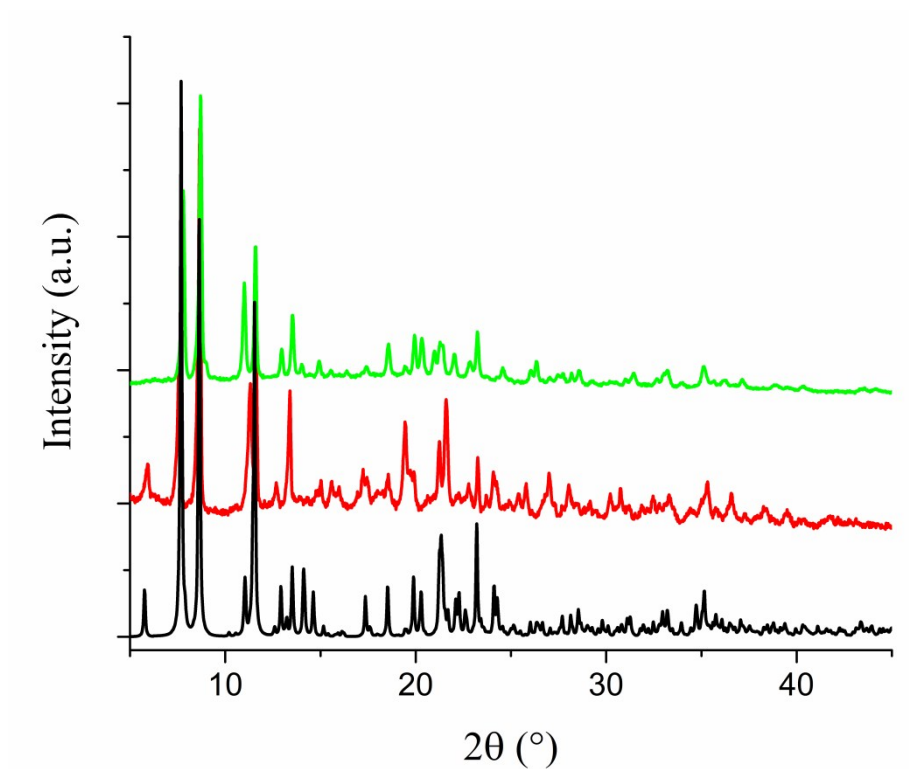


Fig. S14 XRPD patterns of **K[CFA-13]** (green curve), **Cs[CFA-13]** (red curve) and **(Me₂NH₂)[CFA-13]** (black curve).

6. EDX Data

Table S2 Cu/metal ratios for different **M[CFA-13]** samples, calculated from the data shown in Fig. S13-S14.

Sample	Copper/metal ratio
K[CFA-13]	5.62/1
Cs[CFA-13]	5.77/1

Elem	Wt %	At %	K-Ratio	Z	A	F
F K	38.39	66.25	0.1567	1.0527	0.3865	1.0031
K K	6.08	5.10	0.0487	1.0356	0.7661	1.0099
CuK	55.53	28.65	0.5294	0.9472	1.0064	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte. Error	P/B
F K	251.49	0.53	0.71	470.31
K K	110.56	0.15	1.07	723.67
CuK	446.56	0.41	0.53	1096.09

Fig. S15 EDX data for **K[CFA-13]**.

Elem	Wt %	At %	K-Ratio	Z	A	F
F K	29.70	62.13	0.1427	1.0823	0.4429	1.0025
CsL	18.70	5.59	0.1792	0.8702	1.0738	1.0252
CuK	51.60	32.27	0.4861	0.9788	0.9625	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte. Error	P/B
F K	272.60	0.38	0.70	725.75
CsL	139.32	0.52	0.98	266.31
CuK	487.91	0.21	0.52	2273.25

Fig. S16 EDX data for **Cs[CFA-13]**.

7. Crystallographic data

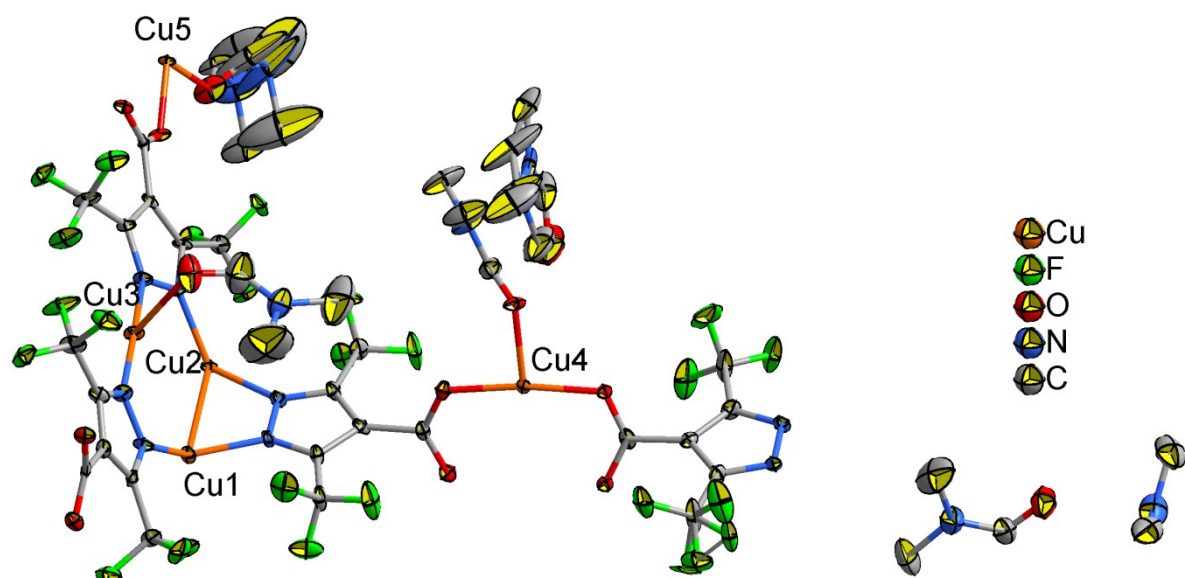


Fig. S17 Ortep-style plot of the asymmetric unit of $(\text{Me}_2\text{NH}_2)[\text{Cu}^{\text{I}}_3\text{Cu}^{\text{II}}_2(\text{tfpc})_4 \cdot 3\text{DMF}] \cdot 2.25\text{DMF}$. Thermal ellipsoids probability: 50 %. Disordered DMF was omitted for clarity.

Table S3 Atomic coordinates ($\times 10^4$) and equivalent isotropic atomic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Me}_2\text{NH}_2)[\text{Cu}^{\text{I}}_3\text{Cu}^{\text{II}}_2(\text{tfpc})_4 \cdot 3\text{DMF}] \cdot 2.25\text{DMF}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	11942(1)	1021(1)	10331(1)	13(1)
F(1)	11067(2)	800(2)	12117(2)	29(1)
O(1)	10714(2)	-1221(3)	12352(2)	16(1)
N(1)	11733(2)	-119(3)	10840(2)	16(1)
C(1)	11326(2)	-276(4)	11282(2)	13(1)
Cu(2)	12830(1)	1004(1)	9338(1)	13(1)
F(2)	11021(2)	1353(2)	11165(2)	32(1)
O(2)	10755(2)	-2612(3)	11790(2)	16(1)
N(2)	12000(2)	-991(3)	10711(2)	16(1)
C(2)	11310(2)	-1262(4)	11448(2)	14(1)
Cu(3)	12595(1)	-1051(1)	10069(1)	16(1)
F(3)	10364(1)	329(3)	11482(2)	34(1)
O(3)	14427(2)	-2691(3)	8380(2)	14(1)
N(3)	13226(2)	-994(3)	9468(2)	15(1)
C(3)	11742(2)	-1683(4)	11069(3)	18(1)
Cu(4)	9943(1)	1604(1)	7082(1)	10(1)
F(4)	11968(2)	-3150(2)	11601(2)	29(1)
O(4)	14711(2)	-1217(2)	8021(2)	17(1)
N(4)	13299(2)	-165(3)	9118(2)	13(1)
C(4)	11927(3)	-2719(4)	11032(3)	25(1)
Cu(5)	15243(1)	-1698(1)	7377(1)	11(1)
F(5)	12461(2)	-2818(3)	10767(2)	44(1)
O(5)	10461(2)	2902(3)	8152(2)	19(1)
N(5)	11621(2)	1392(3)	9505(2)	13(1)
C(5)	10944(3)	544(4)	11513(3)	21(1)
F(6)	11547(2)	-3259(2)	10685(2)	38(1)
O(6)	10515(2)	1375(3)	7768(2)	16(1)
N(6)	12034(2)	1418(3)	9042(2)	15(1)
C(6)	13606(2)	-1663(4)	9243(3)	15(1)
F(7)	13332(2)	-2717(3)	10064(2)	41(1)
O(7)	10113(2)	196(3)	6705(2)	20(1)
N(7)	8122(2)	3327(3)	5135(2)	15(1)
C(7)	13934(2)	-1291(4)	8743(2)	12(1)
F(8)	14200(2)	-2925(3)	9672(2)	34(1)
O(8)	9360(2)	2010(3)	6448(2)	16(1)

	x	y	z	U(eq)
N(8)	7697(2)	3315(3)	5586(2)	16(1)
C(8)	13718(2)	-332(4)	8689(2)	12(1)
F(9)	13417(2)	-3357(2)	9143(2)	36(1)
O(9)	9084(2)	3330(3)	7004(2)	17(1)
N(9)	10827(2)	-925(4)	6546(3)	44(2)
C(9)	10896(2)	-1737(4)	11905(2)	14(1)
F(10)	14455(1)	743(2)	8285(2)	21(1)
O(10)	12412(2)	46(4)	4780(3)	53(1)
N(10)	12936(3)	-167(5)	5683(3)	53(2)
C(10)	13879(2)	454(4)	8225(3)	18(1)
F(11)	13804(1)	166(2)	7629(1)	25(1)
O(11)	12047(2)	-2182(4)	9369(3)	54(1)
N(11)	11320(3)	-1399(5)	8806(3)	56(2)
C(11)	13645(3)	-2662(4)	9525(3)	25(1)
F(12)	13551(1)	1255(2)	8311(2)	23(1)
C(12)	14396(2)	-1770(4)	8353(2)	12(1)
F(13)	10483(2)	829(3)	9981(2)	40(1)
C(13)	11748(2)	1647(4)	8503(3)	16(1)
F(14)	10527(2)	2370(3)	10041(2)	44(1)
C(14)	11144(2)	1805(4)	8601(2)	15(1)
F(15)	10051(2)	1688(4)	9272(2)	55(1)
C(15)	11092(2)	1618(4)	9244(2)	15(1)
F(16)	11743(2)	2055(4)	7428(2)	51(1)
C(16)	12084(2)	1728(4)	7893(3)	22(1)
F(17)	12550(1)	2332(3)	7939(2)	30(1)
C(17)	10538(2)	1652(5)	9632(3)	23(1)
F(18)	12312(2)	871(3)	7710(2)	46(1)
C(18)	10642(3)	-30(4)	6599(3)	28(1)
F(19)	9671(2)	3418(4)	5383(2)	53(1)
C(19)	11446(4)	-1143(6)	6372(5)	72(3)
F(20)	9376(2)	2106(4)	4948(2)	64(1)
C(20)	10430(4)	-1744(6)	6673(5)	73(3)
F(21)	9178(2)	3468(4)	4504(2)	54(1)
C(21)	8647(2)	3107(4)	5423(3)	19(1)
F(22)	7854(2)	2372(3)	7129(2)	36(1)
C(22)	8575(2)	2961(4)	6060(2)	14(1)
C(24)	9041(2)	2742(4)	6548(2)	13(1)
C(25)	9213(3)	3042(6)	5064(3)	39(2)

	x	y	z	U(eq)
F(23A)	7432(5)	3636(9)	7005(5)	45(3)
F(23B)	7688(5)	4000(7)	7083(5)	30(2)
C(27)	11855(4)	-1750(7)	8890(5)	74(3)
N(12)	8463(3)	-476(4)	6049(3)	60(2)
C(28)	11122(6)	-921(8)	8236(6)	107(4)
C(30)	12662(3)	381(6)	5254(3)	40(2)
C(29)	10893(6)	-1490(12)	9307(7)	149(7)
O(1A)	13879(3)	-2740(4)	11492(4)	84(2)
C(42A)	13544(8)	-2094(10)	11708(10)	77(6)
C(43A)	13228(11)	-451(15)	11876(15)	103(9)
N(1A)	13643(9)	-1147(10)	11636(10)	56(5)
C(44A)	14133(11)	-751(18)	11299(19)	135(18)
C(42B)	14119(8)	-2052(9)	11187(8)	61(5)
N(1B)	13989(7)	-1126(9)	11261(7)	39(4)
C(43B)	13519(13)	-747(17)	11658(17)	101(12)
C(44B)	14281(8)	-403(12)	10881(9)	61(5)
C(34)	15592(8)	1597(9)	6733(8)	146(9)
C(36)	15783(5)	-90(7)	6654(6)	60(3)
F(24A)	7058(3)	3061(8)	6654(4)	35(2)
F(24B)	7093(4)	2344(9)	6565(4)	53(3)
C(50B)	7596(5)	2854(8)	6687(5)	20(2)
C(23B)	7960(9)	3005(14)	6139(10)	18(7)
N(0AA)	15000	0	5000	198(19)
C(1AA)	15370(30)	360(60)	4430(40)	210(30)
O(2AA)	15800(20)	-520(40)	4440(30)	200(20)
C(3AA)	15470(20)	-870(40)	5120(30)	210(20)
C(33B)	15590(20)	-10(40)	5212(15)	69(14)
C(50A)	7650(5)	3177(9)	6776(7)	20(2)
C(23A)	7971(8)	3178(14)	6144(9)	12(6)
O(12)	15395(2)	-307(3)	6990(2)	40(1)
N(13A)	15912(5)	818(7)	6455(6)	105(5)
C(36B)	15353(17)	-370(30)	6392(9)	52(11)
C(33)	16403(10)	1001(15)	6024(13)	209(16)
N(13B)	15592(14)	150(20)	5897(13)	51(9)

Table S4 Bond lengths (Å) for (Me₂NH₂)[Cu^I₃Cu^{II}₂(tfpc)₄·3DMF]·**2.25DMF**.

Cu(1)-N(5)	1.954(4)	N(9)-C(19)	1.467(9)
Cu(1)-N(1)	1.955(4)	F(10)-C(10)	1.354(6)
Cu(1)-N(8)#1	1.989(4)	O(10)-C(30)	1.233(8)
Cu(1)-Cu(2)	2.9070(9)	N(10)-C(30)	1.324(9)
F(1)-C(5)	1.352(7)	N(10)-C(31)	1.442(10)
O(1)-C(9)	1.252(6)	N(10)-C(32)	1.476(11)
O(1)-Cu(4)#2	1.977(3)	C(10)-F(12)	1.332(6)
N(1)-C(1)	1.331(6)	C(10)-F(11)	1.333(6)
N(1)-N(2)	1.365(6)	O(11)-C(27)	1.248(10)
C(1)-C(2)	1.395(7)	N(11)-C(27)	1.301(10)
C(1)-C(5)	1.496(7)	N(11)-C(28)	1.439(12)
Cu(2)-N(6)	1.967(4)	N(11)-C(29)	1.440(12)
Cu(2)-N(4)	1.973(4)	F(13)-C(17)	1.353(7)
Cu(2)-N(7)#1	2.023(4)	C(13)-C(14)	1.386(7)
F(2)-C(5)	1.342(6)	C(13)-C(16)	1.504(7)
O(2)-C(9)	1.261(6)	F(14)-C(17)	1.311(7)
O(2)-Cu(5)#3	1.944(3)	C(14)-C(15)	1.391(7)
N(2)-C(3)	1.346(7)	C(14)-C(45)	1.493(7)
N(2)-Cu(3)	1.915(4)	F(15)-C(17)	1.325(6)
C(2)-C(3)	1.387(7)	C(15)-C(17)	1.495(7)
C(2)-C(9)	1.496(7)	F(16)-C(16)	1.319(7)
Cu(3)-N(3)	1.911(4)	C(16)-F(17)	1.334(6)
F(3)-C(5)	1.332(7)	C(16)-F(18)	1.338(7)
O(3)-C(12)	1.265(6)	F(19)-C(25)	1.327(8)
O(3)-Cu(4)#4	1.975(3)	F(20)-C(25)	1.355(9)
N(3)-C(6)	1.340(6)	F(21)-C(25)	1.323(7)
N(3)-N(4)	1.365(6)	C(21)-C(22)	1.375(7)
C(3)-C(4)	1.480(8)	C(21)-C(25)	1.487(8)
Cu(4)-O(8)	1.946(4)	F(22)-C(50B)	1.281(10)

Cu(4)-O(6)	1.953(4)	F(22)-C(50A)	1.406(10)
Cu(4)-O(7)	2.122(4)	C(22)-C(23B)	1.39(2)
Cu(4)-Cu(5)#5	2.6270(9)	C(22)-C(23A)	1.40(2)
F(4)-C(4)	1.344(7)	C(22)-C(24)	1.493(7)
O(4)-C(12)	1.254(6)	F(23A)-C(50B)	1.319(17)
O(4)-Cu(5)	1.936(3)	F(23B)-C(50A)	1.303(18)
N(4)-C(8)	1.330(6)	N(12)-C(38)	1.454(10)
C(4)-F(5)	1.332(6)	N(12)-C(37)	1.498(10)
C(4)-F(6)	1.342(7)	O(1A)-C(42A)	1.249(15)
Cu(5)-O(9)#4	1.990(4)	O(1A)-C(42B)	1.265(14)
Cu(5)-O(5)#4	2.001(4)	C(42A)-N(1A)	1.325(16)
Cu(5)-O(12)	2.101(4)	C(43A)-N(1A)	1.427(17)
O(5)-C(45)	1.243(6)	N(1A)-C(44A)	1.420(17)
N(5)-C(15)	1.338(7)	C(42B)-N(1B)	1.310(14)
N(5)-N(6)	1.354(6)	N(1B)-C(44B)	1.435(15)
O(6)-C(45)	1.260(6)	N(1B)-C(43B)	1.448(16)
N(6)-C(13)	1.341(7)	C(34)-N(13A)	1.416(13)
C(6)-C(7)	1.391(7)	C(36)-O(12)	1.167(10)
C(6)-C(11)	1.496(8)	C(36)-N(13A)	1.344(13)
F(7)-C(11)	1.346(6)	F(24A)-C(50A)	1.356(11)
O(7)-C(18)	1.245(7)	F(24B)-C(50B)	1.349(11)
N(7)-C(21)	1.354(7)	C(50B)-C(23B)	1.44(2)
N(7)-N(8)	1.355(6)	N(0AA)-C(1AA)	1.55(7)
C(7)-C(8)	1.403(7)	N(0AA)-C(1AA)#6	1.55(7)
C(7)-C(12)	1.482(7)	N(0AA)-C(3AA)#6	1.60(5)
F(8)-C(11)	1.328(7)	N(0AA)-C(3AA)	1.60(5)
O(8)-C(24)	1.250(6)	C(1AA)-O(2AA)	1.55(8)
N(8)-C(23A)	1.34(2)	O(2AA)-C(3AA)	1.70(7)
N(8)-C(23B)	1.37(2)	C(33B)-N(13B)	1.467(19)
C(8)-C(10)	1.503(7)	C(50A)-C(23A)	1.53(2)

F(9)-C(11)	1.348(7)	O(12)-C(36B)	1.273(19)
O(9)-C(24)	1.260(6)	N(13A)-C(33)	1.459(14)
N(9)-C(18)	1.298(8)	C(36B)-N(13B)	1.379(19)
N(9)-C(20)	1.456(9)	N(13B)-C(34B)	1.47(6)

Table S5 Bond angles (°) for **(Me₂NH₂)[Cu^I₃Cu^{II}₂(tfpc)₄·3DMF]·2.25DMF**.

N(5)-Cu(1)-N(1)	127.82(18)	C(30)-N(10)-C(31)	121.1(7)
N(5)-Cu(1)-N(8)#1	115.43(18)	C(30)-N(10)-C(32)	119.9(7)
N(1)-Cu(1)-N(8)#1	114.96(18)	C(31)-N(10)-C(32)	119.0(8)
N(5)-Cu(1)-Cu(2)	66.56(12)	F(12)-C(10)-F(11)	107.8(4)
N(1)-Cu(1)-Cu(2)	124.15(12)	F(12)-C(10)-F(10)	105.8(4)
N(8)#1-Cu(1)-Cu(2)	67.38(12)	F(11)-C(10)-F(10)	106.7(4)
C(9)-O(1)-Cu(4)#2	123.9(3)	F(12)-C(10)-C(8)	111.4(4)
C(1)-N(1)-N(2)	107.7(4)	F(11)-C(10)-C(8)	112.3(4)
C(1)-N(1)-Cu(1)	133.3(4)	F(10)-C(10)-C(8)	112.5(4)
N(2)-N(1)-Cu(1)	118.7(3)	C(27)-N(11)-C(28)	124.0(9)
N(1)-C(1)-C(2)	110.6(4)	C(27)-N(11)-C(29)	118.9(9)
N(1)-C(1)-C(5)	120.4(5)	C(28)-N(11)-C(29)	117.1(9)
C(2)-C(1)-C(5)	128.9(5)	F(8)-C(11)-F(7)	106.3(5)
N(6)-Cu(2)-N(4)	129.87(18)	F(8)-C(11)-F(9)	107.3(4)
N(6)-Cu(2)-N(7)#1	114.90(17)	F(7)-C(11)-F(9)	105.8(4)
N(4)-Cu(2)-N(7)#1	113.26(18)	F(8)-C(11)-C(6)	113.2(5)
N(6)-Cu(2)-Cu(1)	66.76(12)	F(7)-C(11)-C(6)	111.1(4)
N(4)-Cu(2)-Cu(1)	123.10(12)	F(9)-C(11)-C(6)	112.6(5)
N(7)#1-Cu(2)-Cu(1)	67.08(12)	O(4)-C(12)-O(3)	126.6(5)
C(9)-O(2)-Cu(5)#3	119.1(3)	O(4)-C(12)-C(7)	116.3(5)
C(3)-N(2)-N(1)	108.2(4)	O(3)-C(12)-C(7)	117.1(4)
C(3)-N(2)-Cu(3)	132.5(4)	N(6)-C(13)-C(14)	111.6(5)
N(1)-N(2)-Cu(3)	119.3(3)	N(6)-C(13)-C(16)	120.6(5)
C(3)-C(2)-C(1)	103.8(4)	C(14)-C(13)-C(16)	127.8(5)
C(3)-C(2)-C(9)	129.3(5)	C(13)-C(14)-C(15)	102.0(5)
C(1)-C(2)-C(9)	126.9(5)	C(13)-C(14)-C(45)	129.1(5)
N(3)-Cu(3)-N(2)	174.02(19)	C(15)-C(14)-C(45)	128.8(5)
C(12)-O(3)-Cu(4)#4	120.3(3)	N(5)-C(15)-C(14)	111.4(4)
C(6)-N(3)-N(4)	107.2(4)	N(5)-C(15)-C(17)	121.1(5)

C(6)-N(3)-Cu(3)	133.1(4)	C(14)-C(15)-C(17)	127.5(5)
N(4)-N(3)-Cu(3)	119.3(3)	F(16)-C(16)-F(17)	106.9(5)
N(2)-C(3)-C(2)	109.8(5)	F(16)-C(16)-F(18)	107.5(5)
N(2)-C(3)-C(4)	121.5(5)	F(17)-C(16)-F(18)	105.4(4)
C(2)-C(3)-C(4)	128.7(5)	F(16)-C(16)-C(13)	112.0(4)
O(8)-Cu(4)-O(6)	172.16(15)	F(17)-C(16)-C(13)	112.4(5)
O(8)-Cu(4)-O(3)#5	89.75(15)	F(18)-C(16)-C(13)	112.2(5)
O(6)-Cu(4)-O(3)#5	88.89(15)	F(14)-C(17)-F(15)	109.5(5)
O(8)-Cu(4)-O(1)#2	89.79(15)	F(14)-C(17)-F(13)	105.1(5)
O(6)-Cu(4)-O(1)#2	89.61(15)	F(15)-C(17)-F(13)	105.5(5)
O(3)#5-Cu(4)-O(1)#2	165.55(15)	F(14)-C(17)-C(15)	114.0(5)
O(8)-Cu(4)-O(7)	96.93(15)	F(15)-C(17)-C(15)	111.5(5)
O(6)-Cu(4)-O(7)	90.89(15)	F(13)-C(17)-C(15)	110.7(5)
O(3)#5-Cu(4)-O(7)	97.20(14)	O(7)-C(18)-N(9)	123.6(6)
O(1)#2-Cu(4)-O(7)	97.19(15)	N(7)-C(21)-C(22)	111.4(5)
O(8)-Cu(4)-Cu(5)#5	86.58(11)	N(7)-C(21)-C(25)	121.6(5)
O(6)-Cu(4)-Cu(5)#5	85.61(11)	C(22)-C(21)-C(25)	126.9(5)
O(3)#5-Cu(4)-Cu(5)#5	84.28(10)	C(21)-C(22)-C(23B)	103.8(10)
O(1)#2-Cu(4)-Cu(5)#5	81.28(11)	C(21)-C(22)-C(23A)	102.5(9)
O(7)-Cu(4)-Cu(5)#5	176.18(11)	C(21)-C(22)-C(24)	128.4(5)
C(12)-O(4)-Cu(5)	122.8(3)	C(23B)-C(22)-C(24)	127.7(10)
C(8)-N(4)-N(3)	108.5(4)	C(23A)-C(22)-C(24)	128.7(9)
C(8)-N(4)-Cu(2)	132.8(4)	O(8)-C(24)-O(9)	127.0(5)
N(3)-N(4)-Cu(2)	118.6(3)	O(8)-C(24)-C(22)	116.2(5)
F(5)-C(4)-F(6)	106.2(5)	O(9)-C(24)-C(22)	116.8(5)
F(5)-C(4)-F(4)	106.1(5)	F(21)-C(25)-F(19)	109.1(6)
F(6)-C(4)-F(4)	106.7(4)	F(21)-C(25)-F(20)	105.5(6)
F(5)-C(4)-C(3)	111.9(5)	F(19)-C(25)-F(20)	104.6(5)
F(6)-C(4)-C(3)	112.3(5)	F(21)-C(25)-C(21)	112.8(5)
F(4)-C(4)-C(3)	113.0(5)	F(19)-C(25)-C(21)	112.0(6)

O(4)-Cu(5)-O(2)#7	170.67(15)	F(20)-C(25)-C(21)	112.3(6)
O(4)-Cu(5)-O(9)#4	89.81(15)	O(11)-C(27)-N(11)	126.6(9)
O(2)#7-Cu(5)-O(9)#4	89.03(15)	C(38)-N(12)-C(37)	114.2(6)
O(4)-Cu(5)-O(5)#4	90.05(15)	O(10)-C(30)-N(10)	123.4(7)
O(2)#7-Cu(5)-O(5)#4	88.55(15)	O(1A)-C(42A)-N(1A)	123.2(18)
O(9)#4-Cu(5)-O(5)#4	164.15(15)	C(42A)-N(1A)-C(44A)	124(2)
O(4)-Cu(5)-O(12)	93.99(16)	C(42A)-N(1A)-C(43A)	120.0(18)
O(2)#7-Cu(5)-O(12)	95.34(17)	C(44A)-N(1A)-C(43A)	115.6(17)
O(9)#4-Cu(5)-O(12)	96.65(18)	O(1A)-C(42B)-N(1B)	124.3(16)
O(5)#4-Cu(5)-O(12)	99.18(18)	C(42B)-N(1B)-C(44B)	119.8(15)
O(4)-Cu(5)-Cu(4)#4	83.83(11)	C(42B)-N(1B)-C(43B)	125.4(19)
O(2)#7-Cu(5)-Cu(4)#4	86.84(11)	C(44B)-N(1B)-C(43B)	114.5(15)
O(9)#4-Cu(5)-Cu(4)#4	81.45(11)	O(12)-C(36)-N(13A)	126.1(9)
O(5)#4-Cu(5)-Cu(4)#4	82.78(11)	F(22)-C(50B)-F(23A)	99.7(9)
O(12)-Cu(5)-Cu(4)#4	177.09(14)	F(22)-C(50B)-F(24B)	104.1(9)
C(15)-N(5)-N(6)	107.6(4)	F(23A)-C(50B)-F(24B)	106.4(11)
C(15)-N(5)-Cu(1)	138.3(4)	F(22)-C(50B)-C(23B)	114.1(12)
N(6)-N(5)-Cu(1)	114.0(3)	F(23A)-C(50B)-C(23B)	117.3(12)
F(3)-C(5)-F(2)	106.6(4)	F(24B)-C(50B)-C(23B)	113.5(12)
F(3)-C(5)-F(1)	107.2(4)	N(8)-C(23B)-C(22)	109.1(14)
F(2)-C(5)-F(1)	106.2(5)	N(8)-C(23B)-C(50B)	119.4(15)
F(3)-C(5)-C(1)	112.1(5)	C(22)-C(23B)-C(50B)	131.4(16)
F(2)-C(5)-C(1)	111.2(4)	C(1AA)-N(0AA)-C(1AA)#6	180(5)
F(1)-C(5)-C(1)	113.0(5)	C(1AA)-N(0AA)-C(3AA)#6	89(3)
C(45)-O(6)-Cu(4)	120.6(3)	C(1AA)#6-N(0AA)-C(3AA)#6	91(3)
C(13)-N(6)-N(5)	107.4(4)	C(1AA)-N(0AA)-C(3AA)	91(3)
C(13)-N(6)-Cu(2)	139.7(4)	C(1AA)#6-N(0AA)-C(3AA)	89(3)
N(5)-N(6)-Cu(2)	112.6(3)	C(3AA)#6-N(0AA)-C(3AA)	180.000(12)
N(3)-C(6)-C(7)	111.2(5)	N(0AA)-C(1AA)-O(2AA)	94(5)
N(3)-C(6)-C(11)	121.2(4)	C(1AA)-O(2AA)-C(3AA)	87(4)

C(7)-C(6)-C(11)	127.6(5)	N(0AA)-C(3AA)-O(2AA)	87(3)
C(18)-O(7)-Cu(4)	117.9(4)	F(23B)-C(50A)-F(24A)	104.8(12)
C(21)-N(7)-N(8)	107.0(4)	F(23B)-C(50A)-F(22)	113.1(10)
C(21)-N(7)-Cu(2)#8	138.6(4)	F(24A)-C(50A)-F(22)	108.8(9)
N(8)-N(7)-Cu(2)#8	111.7(3)	F(23B)-C(50A)-C(23A)	114.0(11)
C(6)-C(7)-C(8)	102.7(4)	F(24A)-C(50A)-C(23A)	107.5(11)
C(6)-C(7)-C(12)	129.6(5)	F(22)-C(50A)-C(23A)	108.3(12)
C(8)-C(7)-C(12)	127.6(5)	N(8)-C(23A)-C(22)	110.7(14)
C(24)-O(8)-Cu(4)	119.6(3)	N(8)-C(23A)-C(50A)	123.9(14)
C(23A)-N(8)-N(7)	107.7(9)	C(22)-C(23A)-C(50A)	125.2(14)
N(7)-N(8)-C(23B)	107.9(9)	C(36)-O(12)-Cu(5)	126.3(6)
C(23A)-N(8)-Cu(1)#8	133.2(9)	C(36B)-O(12)-Cu(5)	108.6(17)
N(7)-N(8)-Cu(1)#8	113.8(3)	C(36)-N(13A)-C(34)	117.1(9)
N(4)-C(8)-C(7)	110.5(4)	C(36)-N(13A)-C(33)	121.3(11)
N(4)-C(8)-C(10)	119.9(4)	C(34)-N(13A)-C(33)	121.2(12)
C(7)-C(8)-C(10)	129.6(4)	O(12)-C(36B)-N(13B)	134(3)
C(24)-O(9)-Cu(5)#5	123.1(3)	C(36B)-N(13B)-C(33B)	133(3)
C(18)-N(9)-C(20)	121.0(6)	C(36B)-N(13B)-C(34B)	126(4)
C(18)-N(9)-C(19)	121.0(6)	C(33B)-N(13B)-C(34B)	98(3)
C(20)-N(9)-C(19)	117.9(6)	O(5)-C(45)-O(6)	127.7(5)
O(1)-C(9)-O(2)	126.8(5)	O(5)-C(45)-C(14)	117.4(5)
O(1)-C(9)-C(2)	116.8(5)	O(6)-C(45)-C(14)	115.0(5)
O(2)-C(9)-C(2)	116.3(5)		

Table S6 Anisotropic atomic displacement parameters ($\text{\AA}^2 \times 10^3$) for **(Me₂NH₂)[Cu^I₃Cu^{II}₂(tfpc)₄·3DMF]·2.25DMF**. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2(a^*)^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cu(1)	12(1)	17(1)	11(1)	3(1)	3(1)	-1(1)
F(1)	44(2)	23(2)	22(2)	-2(2)	13(2)	4(2)
O(1)	16(2)	19(2)	12(2)	3(2)	5(2)	-3(2)
N(1)	18(2)	17(2)	13(2)	-1(2)	6(2)	0(2)
C(1)	8(3)	17(3)	12(3)	4(2)	2(2)	3(2)
Cu(2)	11(1)	14(1)	12(1)	-1(1)	3(1)	2(1)
F(2)	43(2)	25(2)	30(2)	14(2)	25(2)	14(2)
O(2)	14(2)	19(2)	17(2)	1(2)	7(2)	-3(2)
N(2)	15(2)	17(2)	17(2)	3(2)	6(2)	0(2)
C(2)	9(3)	22(3)	12(3)	4(2)	3(2)	-1(2)
Cu(3)	15(1)	18(1)	15(1)	3(1)	10(1)	2(1)
F(3)	13(2)	51(2)	38(2)	12(2)	11(2)	12(2)
O(3)	14(2)	15(2)	14(2)	-4(2)	4(2)	-2(2)
N(3)	16(2)	16(2)	13(2)	1(2)	7(2)	-1(2)
C(3)	17(3)	22(3)	16(3)	0(2)	5(2)	-3(2)
Cu(4)	8(1)	13(1)	9(1)	2(1)	2(1)	0(1)
F(4)	30(2)	25(2)	32(2)	13(2)	12(2)	8(2)
O(4)	19(2)	12(2)	21(2)	-2(2)	10(2)	2(2)
N(4)	16(2)	8(2)	15(2)	2(2)	5(2)	2(2)
C(4)	26(3)	25(3)	23(3)	3(3)	18(3)	-2(3)
Cu(5)	11(1)	13(1)	10(1)	-1(1)	5(1)	0(1)
F(5)	44(2)	27(2)	63(3)	10(2)	40(2)	11(2)
O(5)	19(2)	19(2)	19(2)	-1(2)	-1(2)	0(2)
N(5)	13(2)	18(2)	8(2)	2(2)	1(2)	0(2)
C(5)	26(3)	22(3)	16(3)	8(2)	12(2)	7(3)
F(6)	58(3)	24(2)	33(2)	-6(2)	6(2)	-8(2)
O(6)	17(2)	15(2)	17(2)	4(2)	0(2)	0(2)
N(6)	14(2)	18(2)	12(2)	-1(2)	0(2)	-1(2)
C(6)	13(3)	15(3)	16(3)	-1(2)	6(2)	2(2)
F(7)	51(2)	31(2)	40(2)	18(2)	36(2)	15(2)
O(7)	15(2)	18(2)	27(2)	-6(2)	4(2)	4(2)
N(7)	11(2)	20(2)	12(2)	0(2)	2(2)	-2(2)
C(7)	10(3)	15(3)	11(3)	-4(2)	0(2)	-4(2)
F(8)	33(2)	35(2)	34(2)	18(2)	14(2)	17(2)
O(8)	15(2)	23(2)	12(2)	0(2)	1(2)	5(2)

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N(8)	10(2)	24(3)	13(2)	-1(2)	3(2)	3(2)
C(8)	11(3)	14(3)	11(3)	-5(2)	7(2)	-4(2)
F(9)	38(2)	16(2)	55(3)	0(2)	20(2)	-4(2)
O(9)	16(2)	21(2)	15(2)	2(2)	1(2)	6(2)
N(9)	32(3)	28(3)	71(5)	2(3)	10(3)	14(3)
C(9)	10(3)	22(3)	10(3)	9(2)	-1(2)	4(2)
F(10)	14(2)	21(2)	29(2)	0(1)	7(1)	-5(1)
O(10)	62(4)	39(3)	57(4)	-1(3)	-24(3)	-1(3)
N(10)	76(5)	44(4)	37(4)	2(3)	-11(3)	15(3)
C(10)	22(3)	16(3)	17(3)	3(2)	6(2)	-2(2)
F(11)	32(2)	34(2)	9(2)	2(1)	3(1)	-2(2)
O(11)	54(3)	61(4)	47(3)	19(3)	-11(3)	-9(3)
N(11)	35(4)	73(5)	60(5)	-4(4)	-11(3)	14(3)
C(11)	22(3)	24(3)	29(3)	3(3)	21(3)	5(3)
F(12)	23(2)	15(2)	32(2)	5(1)	13(2)	8(1)
C(12)	8(3)	18(3)	11(3)	2(2)	-2(2)	-3(2)
F(13)	32(2)	53(2)	34(2)	16(2)	14(2)	-8(2)
C(13)	13(3)	20(3)	16(3)	-1(2)	-1(2)	-5(2)
F(14)	38(2)	48(2)	45(2)	-11(2)	23(2)	2(2)
C(14)	13(3)	19(3)	12(3)	-3(2)	-1(2)	-4(2)
F(15)	10(2)	132(4)	23(2)	15(2)	1(2)	3(2)
C(15)	12(3)	20(3)	14(3)	2(2)	-3(2)	-4(2)
F(16)	20(2)	116(4)	16(2)	20(2)	-1(2)	1(2)
C(16)	12(3)	35(3)	18(3)	3(3)	3(2)	0(3)
F(17)	18(2)	48(2)	25(2)	6(2)	6(1)	-8(2)
C(17)	12(3)	39(4)	17(3)	9(3)	-1(2)	-2(3)
F(18)	54(3)	46(2)	38(2)	-16(2)	28(2)	-4(2)
C(18)	31(4)	23(3)	30(4)	1(3)	0(3)	0(3)
F(19)	11(2)	100(4)	49(3)	35(3)	6(2)	-1(2)
C(19)	42(5)	54(6)	120(9)	-9(5)	20(5)	21(4)
F(20)	57(3)	84(3)	50(3)	11(2)	26(2)	51(3)
C(20)	77(7)	29(4)	115(9)	5(5)	36(6)	8(4)
F(21)	28(2)	104(4)	30(2)	40(2)	18(2)	28(2)
C(21)	16(3)	23(3)	19(3)	7(2)	6(2)	2(2)
F(22)	37(2)	55(2)	17(2)	14(2)	5(2)	-9(2)
C(22)	13(3)	10(3)	18(3)	2(2)	1(2)	0(2)
C(24)	7(3)	23(3)	8(3)	4(2)	4(2)	-6(2)
C(25)	17(3)	75(5)	24(4)	24(4)	5(3)	12(3)

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
F(23A)	52(8)	47(7)	36(6)	3(5)	19(6)	13(6)
F(23B)	46(7)	26(5)	18(4)	-11(4)	18(4)	3(4)
C(27)	51(6)	89(7)	83(8)	21(6)	-5(5)	1(5)
N(12)	79(5)	28(3)	71(5)	0(3)	-32(4)	-8(3)
C(28)	120(10)	75(8)	125(11)	32(7)	-30(8)	0(7)
C(30)	44(4)	38(4)	39(4)	3(3)	3(4)	3(3)
C(29)	132(12)	170(15)	147(13)	36(11)	90(11)	48(11)
O(1A)	105(6)	42(3)	105(6)	-3(4)	-44(4)	-3(3)
C(42A)	94(15)	42(8)	94(16)	-7(9)	-23(11)	-19(8)
C(43A)	91(19)	49(11)	170(30)	-6(15)	35(16)	-7(11)
N(1A)	63(11)	38(7)	68(13)	7(8)	-19(9)	-9(7)
C(44A)	53(16)	38(14)	310(50)	-33(19)	60(20)	-23(12)
C(42B)	86(13)	30(7)	67(12)	-11(7)	-37(9)	15(7)
N(1B)	38(9)	32(6)	48(9)	-13(6)	-21(7)	0(6)
C(43B)	90(20)	29(12)	180(30)	-17(17)	68(19)	-18(13)
C(44B)	51(11)	38(8)	94(15)	-13(8)	-7(9)	-13(8)
C(34)	230(20)	49(8)	164(17)	46(10)	106(16)	65(11)
C(36)	69(8)	32(6)	79(8)	12(5)	33(7)	19(5)
F(24A)	6(4)	85(7)	16(4)	15(5)	3(3)	2(5)
F(24B)	31(5)	95(8)	34(5)	28(6)	-2(4)	-34(6)
O(12)	43(3)	22(2)	54(3)	18(2)	22(3)	-2(2)
N(13A)	116(9)	42(6)	160(13)	33(7)	95(9)	14(6)
C(33)	200(30)	117(16)	320(30)	90(20)	190(30)	3(17)
C(38)	92(7)	42(5)	54(5)	-9(4)	-18(5)	-13(5)
C(37)	55(5)	49(5)	85(7)	-28(5)	-23(5)	2(4)
C(31)	105(8)	50(6)	90(8)	35(5)	28(6)	19(5)
C(32)	169(12)	114(9)	59(7)	-29(7)	-69(8)	53(9)
C(45)	9(3)	25(3)	11(3)	2(2)	1(2)	-3(2)
Cu(1)	12(1)	17(1)	11(1)	3(1)	3(1)	-1(1)
F(1)	44(2)	23(2)	22(2)	-2(2)	13(2)	4(2)
O(1)	16(2)	19(2)	12(2)	3(2)	5(2)	-3(2)
N(1)	18(2)	17(2)	13(2)	-1(2)	6(2)	0(2)
C(1)	8(3)	17(3)	12(3)	4(2)	2(2)	3(2)
Cu(2)	11(1)	14(1)	12(1)	-1(1)	3(1)	2(1)