Electronic Supplementary Information

Reversible guest vapour sorption in breathing crystals of discrete ionic binuclear Cu(I) complex

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1. Experimental procedures:

Materials: *N*-[(*E*)-(4-chlorophenyl)methylidene]-4*H*-1,2,4-triazol-4-amine (**ClPhtrz**) and $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2\cdot 2CH_3CN$ (**1-CH_3CN**) were synthesis and characterized according to the procedures previously described [K. Drabent, Z. Ciunik, P. J. Chmielewski, *Eur. J. Inorg. Chem.*, 2003, 1548-1554; K. Drabent, A. Białońska, Z. Ciunik, *Inorg. Chem. Comm.*, 2004, **7**, 224-227.]

The IR spectra were recorded with a Bruker 113v FTIR spectrometer.

^{1}H NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer

X-Ray data for **1** and for **all 1-guest'** were collected on a Xcalibur with Sapphire2 detector and/or on a Xcalibur with Ruby detector (both with Mo-Kα radiation; λ = 0.71073 Å) and/or on a Xcalibur PX with Onyx detector (Cu-Kα radiation, λ = 1.54175 Å). All the data were collected at 100 K and additionally for **1** at 293 K using an Oxford Cryosystem device. A low ratio of observed/unique reflections for most of **1-guest'** is due to weakly diffracting crystals. Data reduction and analysis were carried out with the CrysAlice 'RED' program (CrysAlis 'RED', Oxford Diffraction Ltd., Abingdon, Oxfordshire, England, 2009). The space groups were determined using the XPREP program (XPREP – data preparation & reciprocal space exploration, Ver. 5.1/NT, Bruker Analytical X-ray System, 1997). Structures were solved by direct methods using the SHELXS program (G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112) and refined using all F^2 data, as implemented by the SHELXL program. In the case of all **1-guest'**, non-hydrogen atoms were refined with anisotropic displacement parameters. Because of too low data completeness and too low ratio of observed/unique reflections, non-hydrogen (except Cu and Cl) atoms in **1** were refined with isotropic displacement parameters. For all **1-guest'** the occupancy factor for target guest molecules were calculated and then fixed with a suitable value. For **1-C_8H_{10},** we assumed that the sum of the occupancy factors of all components of the disordered xylene molecules is equal to 1 and the ratio of particular components of the disorder was refined. Basing on the final Δρ map, it is likely that the disorder of xylene isomers is more complex. Some restraints were applied for disordered units. All H atoms were placed at their calculated positions. Before the last cycle of refinement all H atoms were fixed and were allowed to ride on their parent atoms.

PXRD patterns were recorded on D8 ADVANCE with Vantec detector (Cu-Kα radiation, λ = 1.54175 Å).

1.1. Solid-vapour synthesis and characteristics of $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2\cdot 2$guest' (guest' = methanol, nitromethane, dichloromethane, tetrachloromethane, 1,2-dichloroethane, 2-methylpropan-2-ol, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitilene, naphthalene, durene, (2-butyl)benzene):

Vial in vial technique was applied for guest exchange experiments. **1-CH_3CN** obtained according to the procedures described above in 1.2. and a suitable guest were placed in internal and external vials, respectively. After covering of the external vial, the samples were left for one week allowing the vapour guest exchanging and after one week the solid in the internal vial was analysed:

1.1.1. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2\cdot 2CH_3OH$ (**1-CH_3OH**). IR (in nujol mull): 3113 m, 2360 1653 m, 1616 m, 1593 m, 1566 m, 1522 m, 1521 , 1490 m, 1412 m, 1397 m, 1324 w, 1398 w, 1281 w, 1216 w, 1172 s, 1084 m, 1012 s, 993 s, 976 s, 955 s, 929 s, 884 m, 832 m, 766 w, 668, 624 s, 517 w, 508 w, 455 w; ^{1}H NMR (in CD_3CN): 8.89 (b. s, 2H); 8.83 (s, 1H); 7.87 (d, 2H, J=8.5 Hz); 7.58 (d, 2H, J=8.5Hz); 5.45 (s, 0.04H); 3.54 (quin, 0.10H); Crystal

data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2 \cdot 5.24(CH_3OH)$, M = 1320.00, monoclinic, $P2_1/c$, a = 6.955(2), b = 18.182(3), c = 22.181(3) Å, β = 95.31(3)° V = 2792.9(10) Å^3, Z = 2, D_c = 1.570 Mg m^{-3}, T = 100(2) K, R = 0.054, wR = 0.129 (5024 reflections with $I > 2\sigma(I)$) for 454 variables, CCDC 949080;

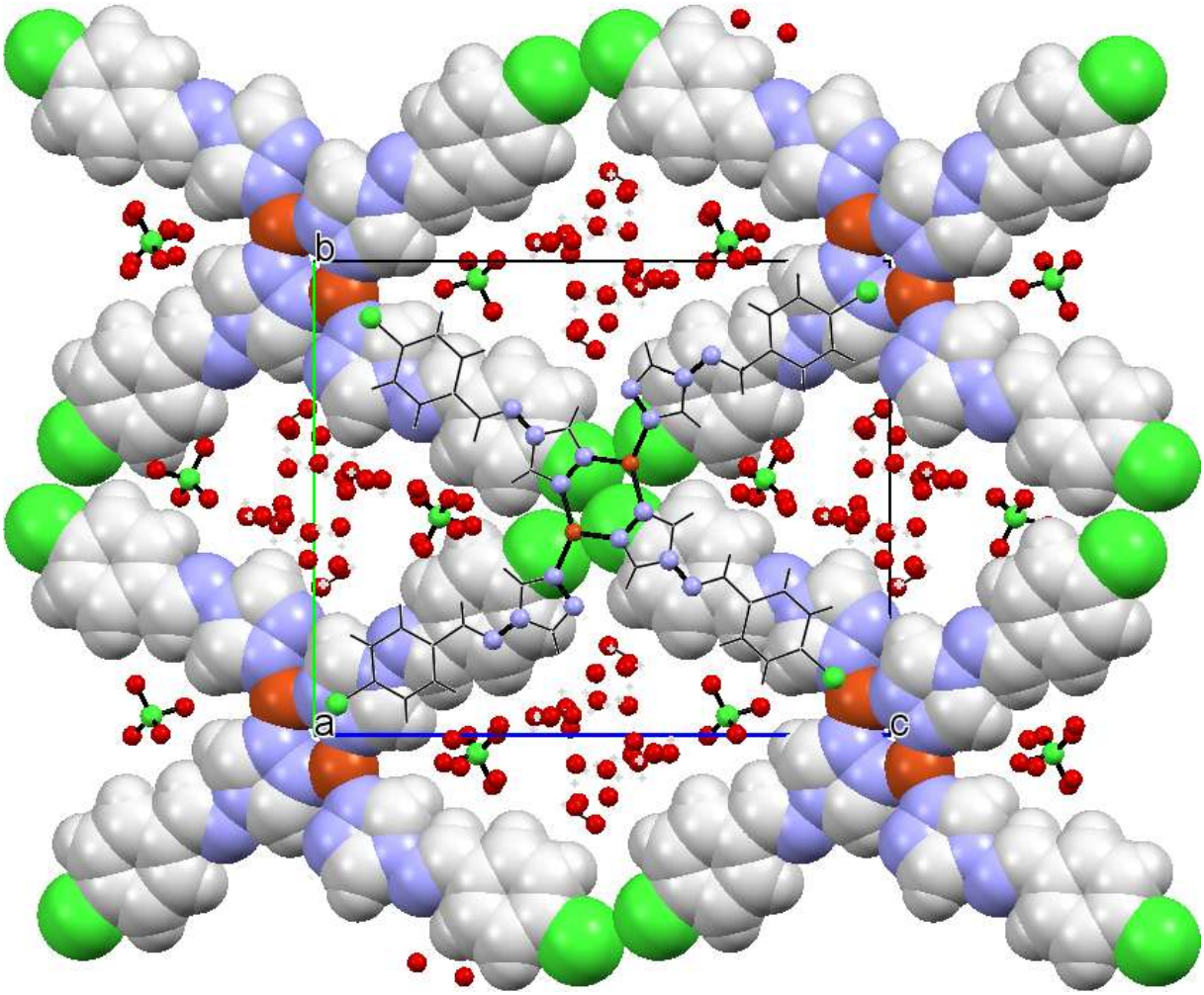


Fig. S1. Packing of **1-CH$_3$OH**

1.1.2. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2 \cdot 2CH_3NO_2$ (**1-CH$_3$NO$_2$**). IR (in KBr disc): 3479 m, 3119 m, 3062 m, 3011 m, 1943 m, 1660 m, 1618 m, 1594 m, 1566 m, 1523 m, 1491 m, 1401 m, 1389 w, 1325 w, 1318 w, 1302 w, 1218 s, 1174 s, 1091 m, 1013 s, 1003 s, 968 s, 944 m, 884 m, 833 m, 764 w, 711 s, 657 s, 624 s, 516 w, 506 w, 456 w, 392 w; ^{1}H NMR (in CD_3CN): 8.88 (b.s, 2H), 8.82 (s, 1H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 4.31 (s, 3H),

1.1.3. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2 \cdot 2CH_2Cl_2$ (**1-CH$_2$Cl$_2$**). IR (in KBr disc): 3436 m, 3117 m, 2369 m. 1649 m, 1617 m, 1584 m, 1526 m, 1493 m, 1411 m, 1399 m, 1339 w, 1318 w, 1301 w, 1283 w, 1214 w, 1173 s, 1083 m, 1039 m, 1004 s, 991 s, 965 s, 942 s, 832 m, 776 w, 764 w,736 s, 624 s, 516 s, 455 w, 392 w; ^{1}H NMR (in CD_3CN): 8.81 (b. s, 2H); 8.80 (s, 1H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 5.36 (s, 0.7H);

1.1.4. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2$ (**1-CCl$_4$**). IR (in KBr disc): 3461 m, 3143 m, 3116 m, 3069 m, 1943 m, 1594m, 1586 m, 1524 m, 1491 m, 1479 m, 1400 m, 1326 w, 1302 w, 1299 w, 1217 w, 1169 s, 1086 m, 1013 s, 1006 s, 1004 s, 972 s, 947 s, 884 m, 876 m, 835 m, 789 w, 764 w, 731 s, 624 s, 516 w, 511 w, 456 w, 390 w; Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2 \cdot 2(CCl_4)$, M = 1460.14, monoclinic, $P2_1/c$, a = 6.971(2), b =

17.912(3), *c* = 22.289(3) Å, *β* = 95.64(3)º *V* = 2769.6(10) Å^3, *Z* = 2, D_c = 1.751 Mg m^{-3}, *T* = 100(2) K, *R* = 0.105, *wR* = 0. 0.131 (1847 reflections with $I > 2\sigma(I)$) for 352 variables, CCDC 949081;

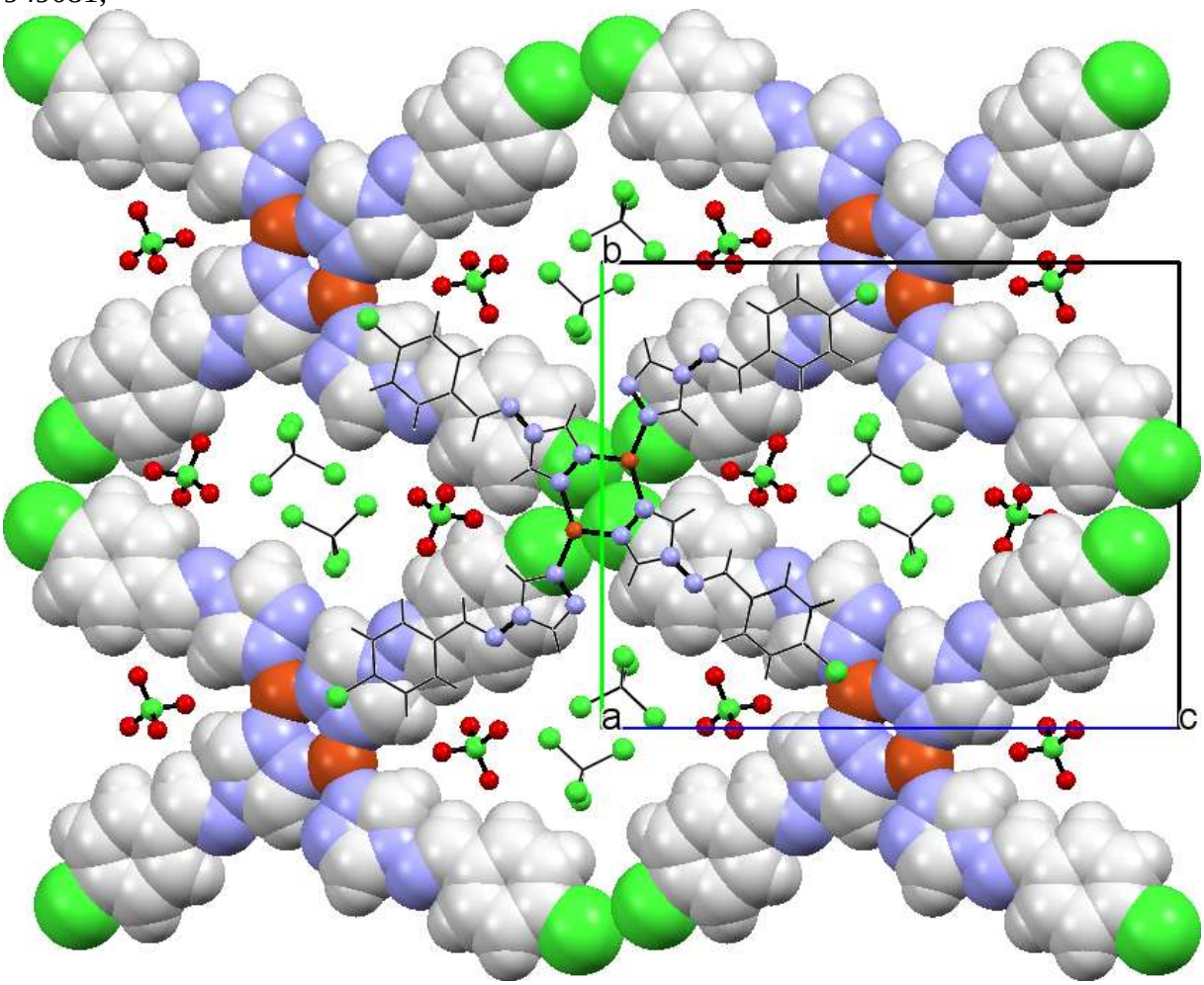


Fig. S2. Packing of **1-CCl$_4$**

1.1.5. [Cu$_2$(*μ*-ClPhtrz)$_2$(ClPhtrz)$_2$](ClO$_4$)$_2$·2 C$_2$H$_4$Cl$_2$ (**1-C$_2$H$_4$Cl$_2$**). IR (in KBr disc): 3437 m, 3115 m, 1618 m, 1593 m, 1565 m, 1522 m, 1491 m, 1430 m, 1413 m, 1399 m, 1324 w, 1300 w, 1283 w, 1215 w, 1170 s, 1085 m, 1059 m, 1013 s, 991 s, 978 s, 951 s, 930 s, 882 m, 831 m, 764 w, 710 s, 669 s, 650 s, 624 s, 516 w, 508 w, 455 w, 410 w, 389 w; ^{1}H NMR (in CD$_3$CN): 8.81 (s, 1H); 8,79 (b. s. 2H);7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 3.81 (s, 2H)

1.1.6. [Cu$_2$(*μ*-ClPhtrz)$_2$(ClPhtrz)$_2$](ClO$_4$)$_2$·2 C$_4$H$_9$OH (**1-C$_4$H$_9$OH**). IR (in KBr disc): 3587 m, 3453 m, 3128 m, 2975 m, 2366 m, 2355 m, 1948 m, 1652 m, 1619 m, 1594 m, 1586 m, 1524 m, 1491 w, 1413 w, 1399 m, 1394 w, 1325 w, 1319 w, 1301 w, 1217 s, 1174 s, 1088 m, 1070 m, 1013 s, 1005 s, 991 s, 968 s, 907 m, 884 m, 831 m, 764 w, 711 s, 669 s, 625 s, 516 w, 457 w, 391 w; ^{1}H NMR (in CD$_3$CN): 8.81 (s, 1H); 8.77 (b. s, 2H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 2.35 (s, 0.4H); 1.17(s, 3.3H);

1.1.7. [Cu$_2$(*μ*-ClPhtrz)$_2$(ClPhtrz)$_2$](ClO$_4$)$_2$·2 C$_6$H$_6$ (**1-C$_6$H$_6$**). IR (in KBr disc): 3435 m, 3118 m, 1617 m, 1592 m, 1566 m, 1517 m, 1491 m, 1413 m, 1398 m, 1324 w, 1300 w, 1283 w, 1215 w, 1169 s, 1085 m, 1059 m, 1013 s, 989 s, 978 s, 955 s, 930 s, 882 m, 834 m, 796 w,

764 w, 710 s, 623 s, 509 w, 485 m, 455 w, 390 w; ^{1}H NMR (in CD_3CN): 8.80 (s, 1H); 8.78 (b.s, 2H) 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.4 (s, 2.5H);

1.1.8. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2{\cdot}2\ C_7H_8$ (**1-C_7H_8**). IR (in KBr disc): 3469 m, 3118 m, 1593 m, 1584 m, 1526 m, 1492 m, 1415 m, 1399 m, 1325 w, 1310 w, 1301 w, 1217 w, 1174 s, 1089 m, 1058 m, 1014 s, 989 s, 969 s, 945 s, 883 m, 836 m, 765 w, 726 w, 696 s, 625 s, 511 w, 455 w, 390 w; ^{1}H NMR (in CD_3CN): 8.80 (s, 1H); 8.78 (b.s, 2H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.25 (t, 1H, J= 7.5 Hz), 7.19 (d, 1H, J = 7.5 Hz), 7.15 (t, 0.5H, J = 7 Hz) 2.33 (s, 3H); Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2{\cdot}2(C_7H_8)$, M = 1336.79, monoclinic, $P2_1/c$, a = 6.999(2), b = 17.994(3), c = 22.019(3) Å, β = 95.67(3)º V = 2759.5(10) Å^3, Z = 2, D_c = 1.609 Mg m^{-3}, T = 100(2) K, R = 0.060, wR = 0.075 (1938 reflections with $I > 2\sigma(I)$) for 370 variables, CCDC 949082;

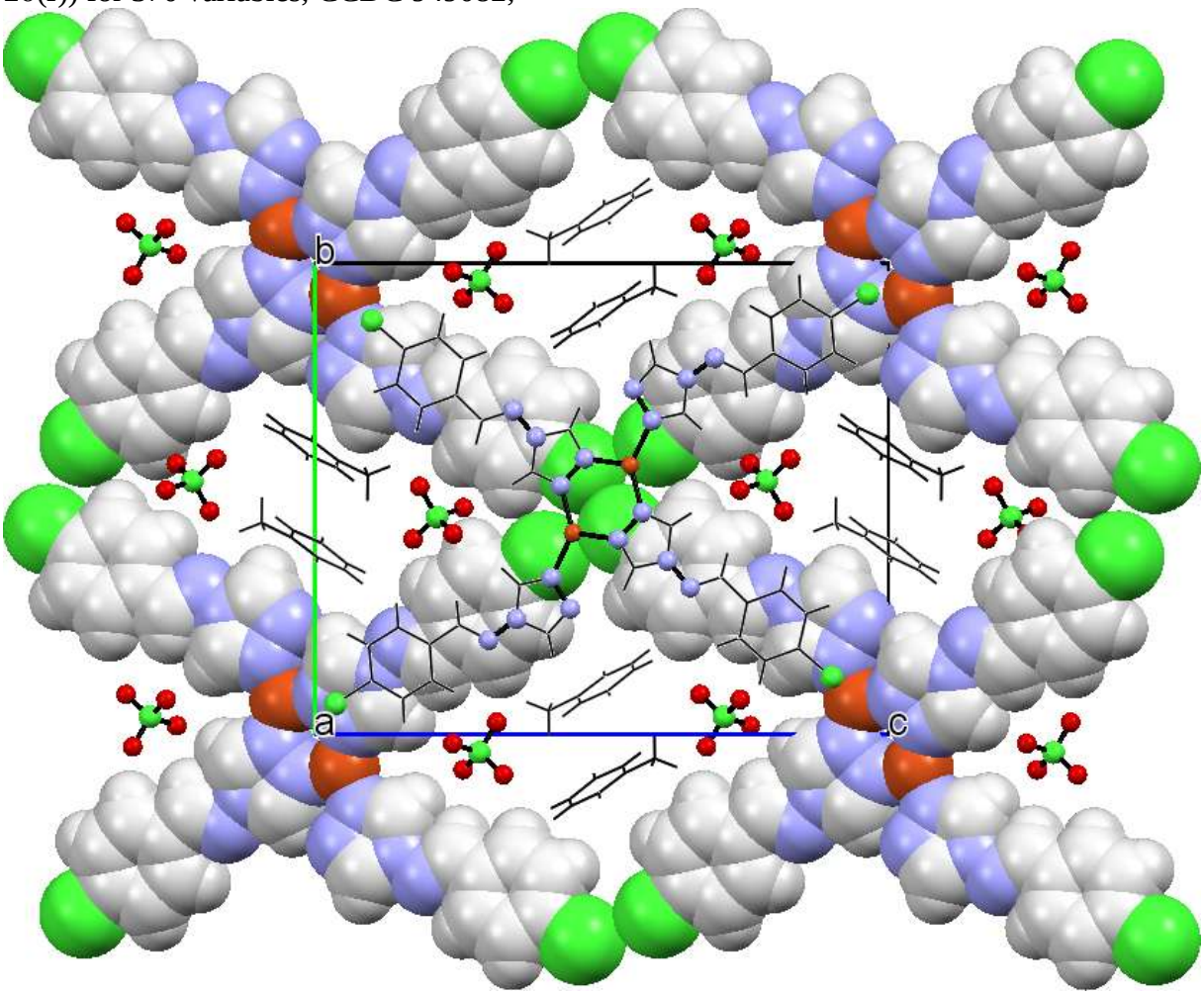


Fig. S3. Packing of **1-C_7H_8**

1.1.9. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2{\cdot}2\ C_8H_{10}$ (**1-*o*-C_8H_{10}**). IR (in KBr disc): 3436 m, 3144 w, 3117 m, 1649 m, 1616 m, 1592 m, 1566 m, 1521 m, 1491 m, 1413 m, 1397 m, 1324 w, 1301 w, 1283 w, 1215 w, 1173 s, 1083 m, 1057 m, 1013 s, 991 s, 977 s, 956 s, 929 s, 883 m, 834 m, 776 w, 764 w, 710 s, 624 s, 510 w, 455 w, 388 w; ^{1}H NMR (in CD_3CN): 8.90 (b.s, 2H); 8.81 (s, 1H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.15-7.08 (m, 2H); 2.25 (s, 3H); Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2{\cdot}2(C_8H_{10})$, M = 1364.84, monoclinic, $P2_1/c$, a = 14.183(3), b = 18.048(3), c = 22.365(4) Å, β = 95.08(3)º V = 5702.4(19) Å^3, Z = 4, D_c = 1.590 Mg m^{-3}, T = 100(2) K, R = 0.041, wR = 0.072 (6587 reflections with $I > 2\sigma(I)$) for 785 variables, CCDC 949083;

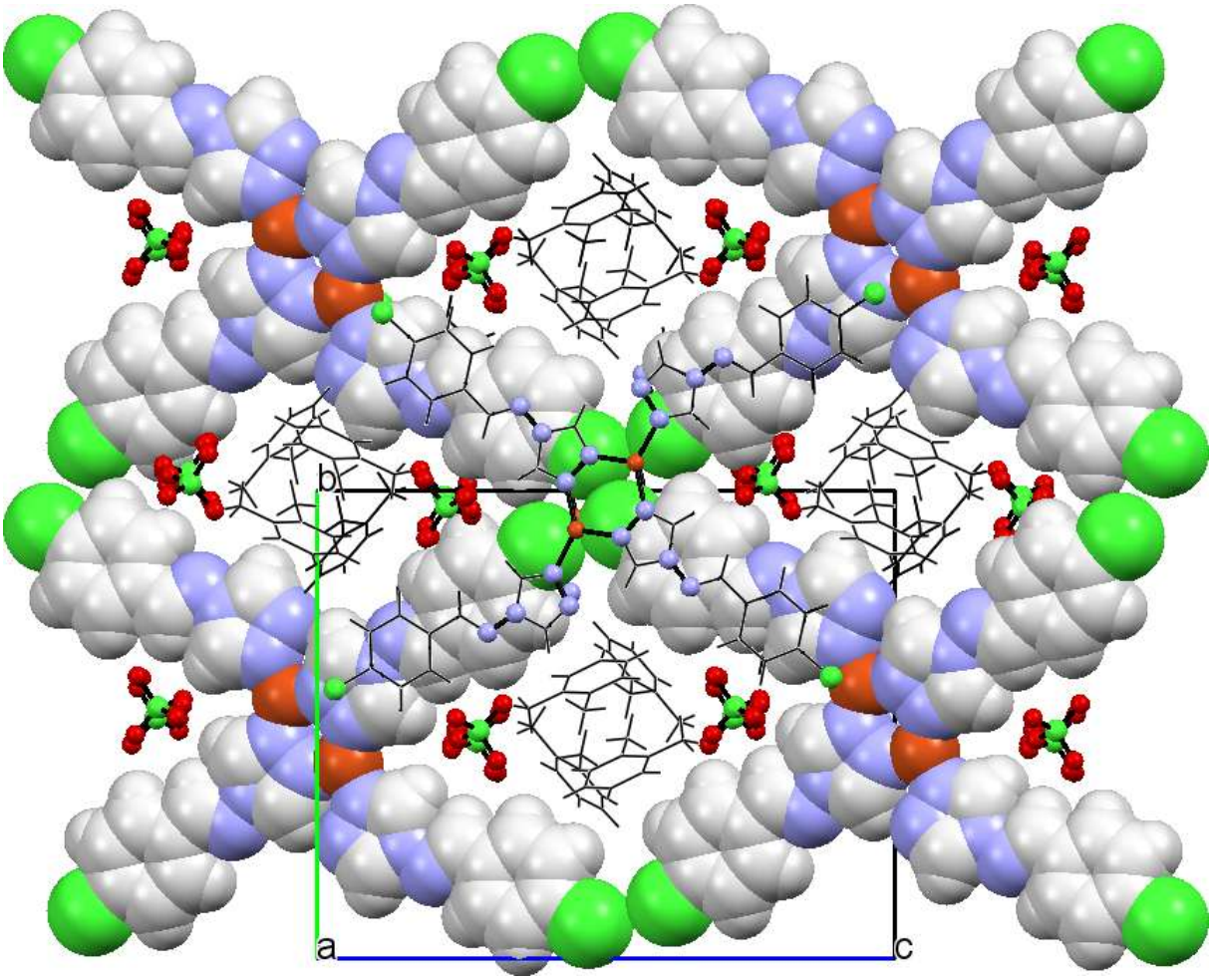


Fig. S4. Packing of **1-*o*-C_8H_{10}**

1.1.10. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2{\cdot}2\ C_8H_{10}$ (**1-*m*-C_8H_{10}**). IR (in KBr disc): 3437 m, 3145 w, 3116 m, 1648 m, 1618 m, 1593 m, 1566 m, 1522 m, 1491 m, 1414 m, 1398 m, 1324 w, 1301 w, 1283 w, 1214 w, 1172 s, 1084 m, 1058 m, 1013 s, 990 s, 977 s, 956 s, 929 s, 883 m, 869 s, 834 m, 776 w, 764 w, 710 s, 693 s, 624 s, 510 w, 455 w, 434 w, 388 w; ; ^{1}H NMR (in CD_3CN): 8.80 (s, 1H), 8.78 (b.s, 2H), 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.15 (t, 0.5H, J=7Hz), 7.03 (s, 0.5H) 6.99 (d, 1H, J=7.5Hz) 2.28 (s, 3H); Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2{\cdot}2(C_8H_{10})$, M = 1364.84, monoclinic, $P2_1/c$, a = 6.987(2), b = 18.534(3), c = 22.097(4) Å, β = 94.78(3)° V = 2851.5(11) Å^3, Z = 2, D_c = 1.590 Mg m^{-3}, T = 100(2) K, R = 0.042, wR = 0.074 (6544 reflections with $I > 2\sigma(I)$) for 380 variables, CCDC 949084;

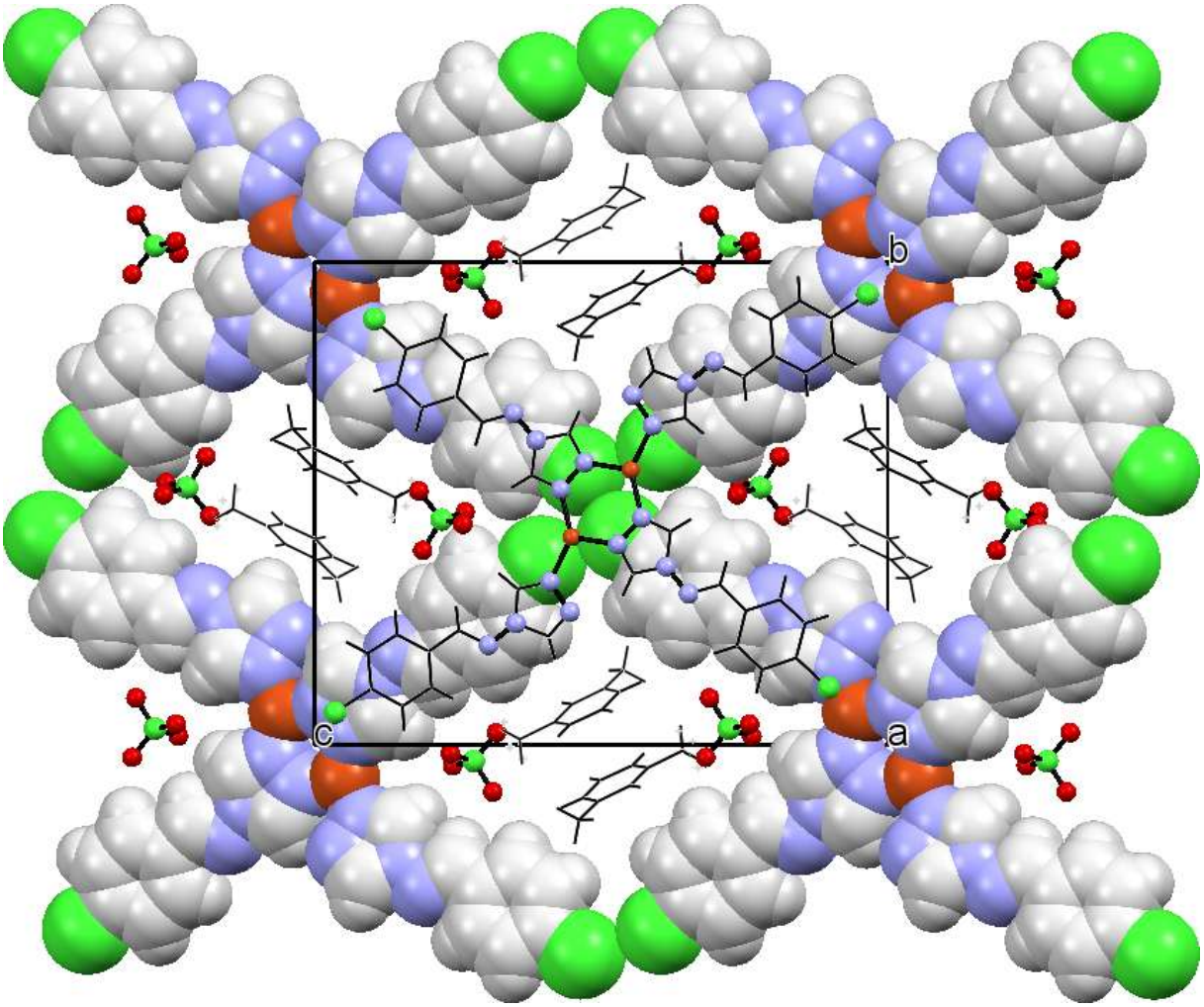


Fig. S5. Packing of **1-*m*-C_8H_{10}**

1.1.11. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2 \cdot 2\ C_8H_{10}$ (**1-*p*-C_8H_{10}**). IR (in KBr disc): 3465 m, 3122 m, 3062 m, 2965 w, 1675 m, 1618 m, 1593 m, 1567 m, 1521 m, 1492 m, 1416 m, 1399 m, 1324 w, 1302 w, 1301 w, 1283 w, 1214 w, 1171 s, 1085 m, 1058 m, 1013 s, 1003 s, 990 s, 977 s, 956 s, 929 s, 882 m, 869 s, 834 m, 776 w, 764 w, 763 w 710 s, 624 s, 516 w 510 w, 455 w, 434 w, 390 w; ^{1}H NMR (in CD_3CN): 8.80 (s, 1H), 8.78 (b.s, 2H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.09 (s, 2H), 2.27 (s, 3H); Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2 \cdot 2(C_8H_{10})$, M = 1364.84, monoclinic, $P2_1/c$, a = 6.946(2), b = 18.278(3), c = 22.450(4) Å, β = 91.75(3)° V = 2848.9(11) Å^3, Z = 2, D_c = 1.591 Mg m^{-3}, T = 100(2) K, R = 0.039, wR = 0.065 (3370 reflections with $I > 2\sigma(I)$) for 408 variables, CCDC 949085;

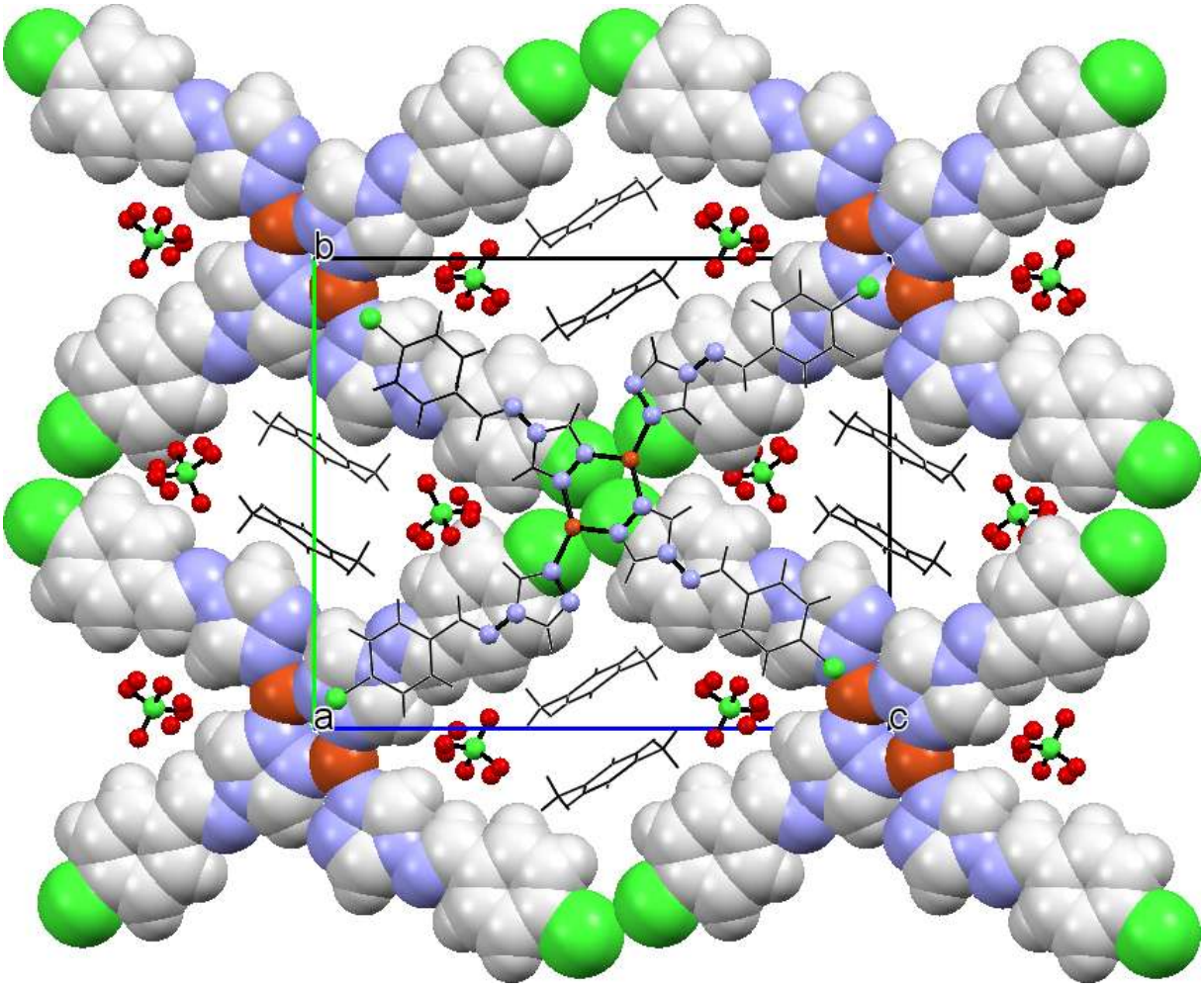


Fig. S6. Packing of **1-*p*-C_8H_{10}**

1.1.12. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2{\cdot}2\ C_9H_{12}$ (**1-C_9H_{12}**). IR (in KBr disc): 3436 m, 3117 m, 1618 m, 1592 m, 1566 m, 1522 m, 1491 m, 1412 m, 1397 m, 1323 w, 1300 w, 1283 w, 1214 w, 1171 s, 1083 m, 1059 m, 1013 s, 976 s, 955 s, 930 s, 881 m, 834 m, 786 m, 764 w, 710 s, 624 s, 509 w, 478 s, 454 w, 389 w; ^{1}H NMR (in CD_3CN): 8.80 (s, 1H), 8.76 (b.s, 2H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 6.80 (s, 1H); 2.26 (s, 3H);

1.1.13. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2{\cdot}2\ C_{10}H_8$ (**1-$C_{10}H_8$**). IR (in KBr disc): 3437 m, 3115 m, 1618 m, 1593 m, 1566 m, 1522 m, 1491 m, 1413 m, 1398 m, 1324 w, 1301 w, 1283 w, 1214 w, 1171 s, 1084 m, 1058 m, 1013 s, 989 s, 977 s, 955 s, 929 s, 882 m, 834 m, 776 w, 764 w, 710 s, 693 s, 624 s, 510 w, 455 w, 435 w, 389 w; ^{1}H NMR (in CD_3CN): 8.82 (b.s, 2H), 8.80 (s, 1H), 7.89 (dd, 1H, J= 6, 3 Hz); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.51 (dd, 1H, J = 6.4, 3 Hz); Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2{\cdot}2(C_{10}H_8)$, M = 1408.85, monoclinic, $P2_1/c$, a = 7.023(2), b = 18.472(3), c = 22.101(4) Å, β = 95.36(3)° V = 2854.6(11) Å^3, Z = 2, D_c = 1.639 Mg m^{-3}, T = 100(2) K, R = 0.120, wR = 0.175 (4762 reflections with $I > 2\sigma(I)$) for 398 variables, CCDC 949086;

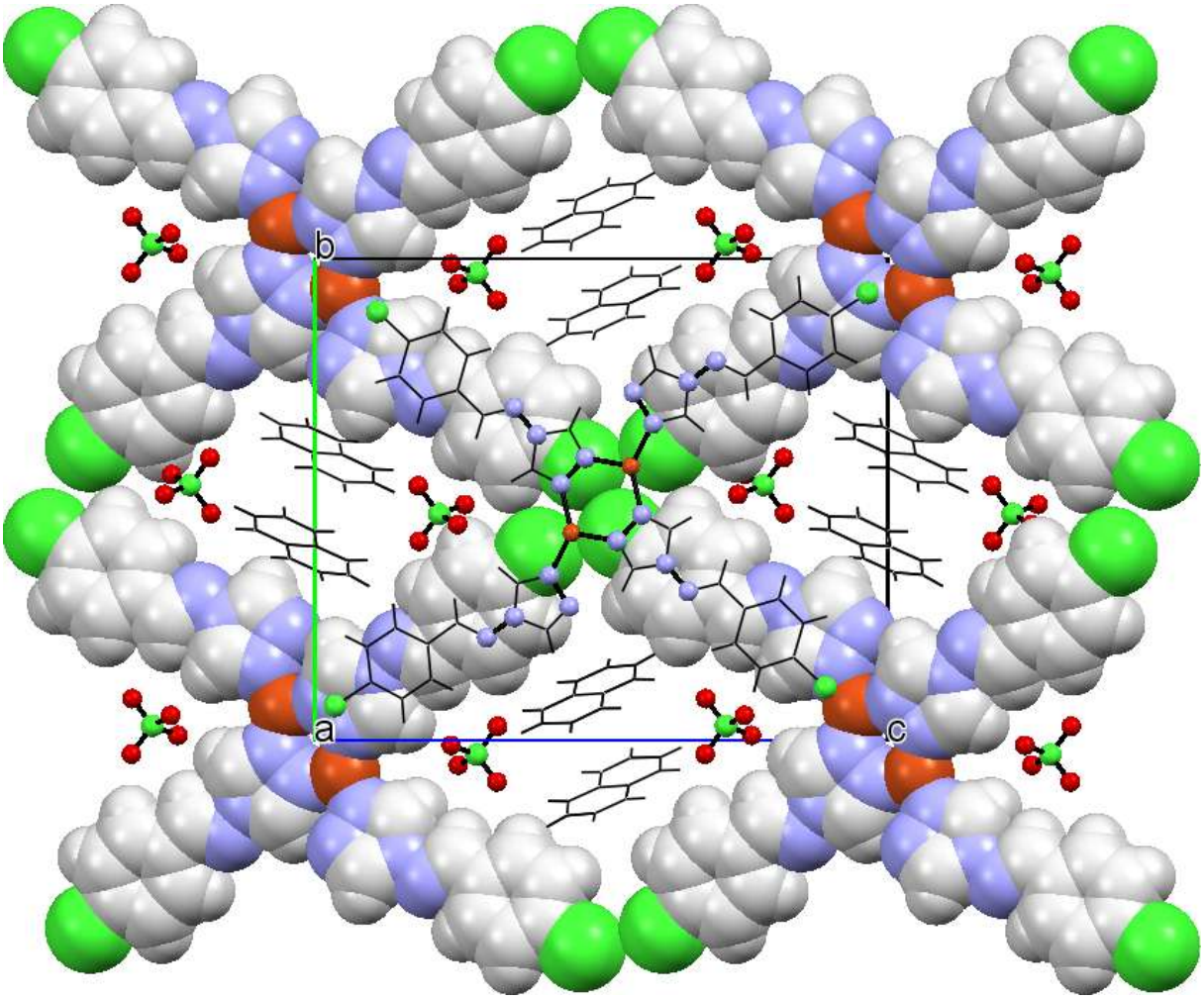


Fig. S7. Packing of **1-$C_{10}H_8$**

1.1.14. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2 \cdot 2\ C_{10}H_{14}$ (**1-$C_{10}H_{14}$ (1)** - durene). IR (in KBr disc): 3466 m, 3119 m, 1614 m, 1596 m, 1567 m, 1525 m, 1491 m, 1411 m, 1399 m, 1325 w, 1302 w, 1283 w, 1215 w, 11716s, 1087 m, 1065 m, 1014 s, 979 s, 969 s, 940 s, 894 m, 834 m, 784 m, 714 w, 710 s, 625 s, 511 w, 489 s, 451 w, 390 w; ^{1}H NMR (in CD_3CN): 9.03 (b.s, 2H), 8.85 (s, 1H), 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 6.88 (s, 0.3H); 2.16 (s, 1.2H)

1.1.15. $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2 \cdot 2\ C_{10}H_{15}$ (**1-$C_{10}H_{14}$(2)** - (2-butyl)benzene). IR (in KBr disc): 3469 m, 3120 m, 3069m, 2971 w, 2960 w, 2905 w, 2389 w, 1684 m, 1620 m, 1594 m, 1566 m, 1526 m, 1492 m, 1400 m, 1326 w, 1319 w, 1295 w, 1218 w, 1171 s, 1088 m, 1068 m, 1013 s, 1001 s, 967 s, 946 s, 884 m,834 m, 764 w, 710 s, 695 s, 625 s, 517 w, 516 w, 456 w, 392 w; ^{1}H NMR (in CD_3CN): 9.01 (b.s, 2H), 8.85 (s, 1H), 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.29 (t, 0.5H, J = 7.5 Hz); 7.21 (d, 0.5H, J = 7.3 Hz); 7.17 (t, 0.25H, J = 7.5 Hz), 2.6 (m, 0.25H); 1.59 (q, 0.5H, J= 7.2 Hz); 1.21 (d, 0.75H, J=6.9 Hz), 0.79 (t, 0.75H, J = 7.3 Hz);

1.2. Separation of xylene isomers: IR (in KBr disc): 3437 m, 3115 m, 2360 w, 1617 m, 1593 m, 1566 m, 1522 m, 1491 m, 1413 m, 1398 m, 1324 w, 1301 w, 1283 w, 1214 w, 1170 s, 1084 m, 1059 m, 1013 s, 989 s, 978 s, 955 s, 929 s, 883 m, 835 m, 764 w, 710 s, 689 s, 510 w, 455 w, 389 w; ^{1}H NMR (in CD_3CN): 8.79 (s, 1H); 8.75 (b. s, 1H); 7.87 (d, 2H, J=8.5 Hz); 7.57 (d, 2H, J=8.5Hz); 7.13 (t, J=7Hz); 7.12 (t, J=6Hz); 7.08 (t, J=4Hz); 7.07(s); 7.07(s); 7.02 (s, 0.3H); 6.97 (d, 0.6H, J=7.8Hz); 2.28 (s, 1.8H); 2.27 (s, 0.8H); 2.25 (s, 1.2H); Crystal data:

$[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2 \cdot 2(C_8H_{10})$, M = 1364.84, monoclinic, $P2_1/c$, a = 6.993(2), b = 18.663(3), c = 22.010(4) Å, β = 95.07(3)º V = 2861.3(11) Å^3, Z = 2, D_c = 1.584 Mg m^{-3}, T = 100(2) K, R = 0.113, wR = 0.176 (5558 reflections with $I > 2\sigma(I)$) for 528 variables, CCDC 949087

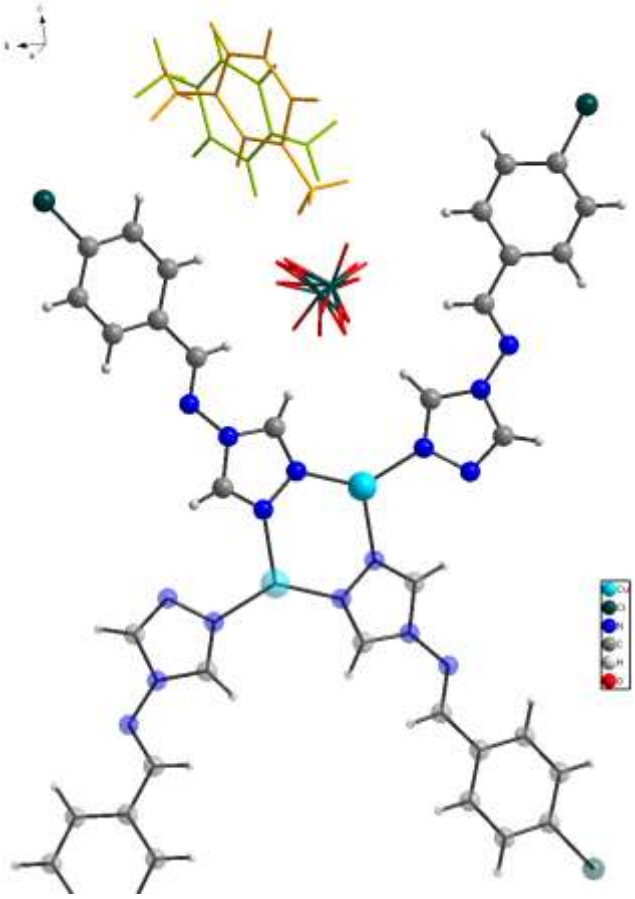
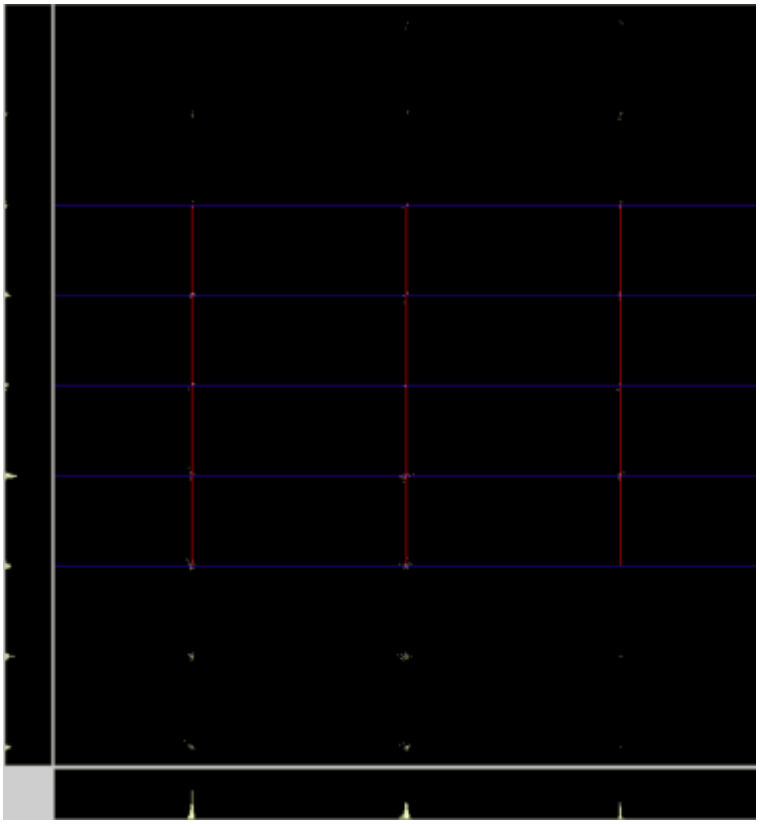
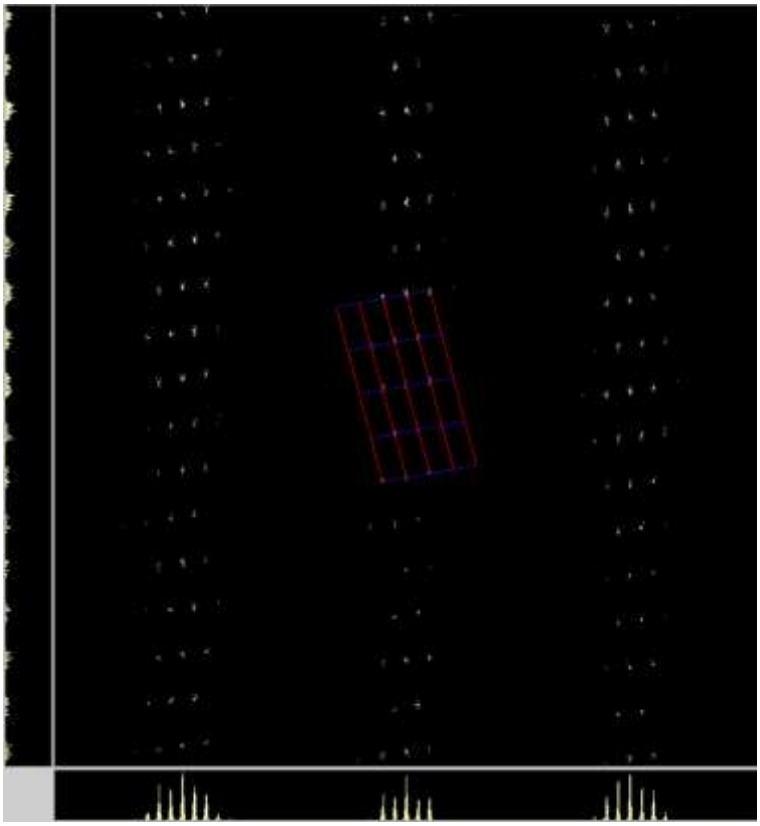


Fig. S8. Packing of **1-C_8H_{10}**; disordered *p*- and *m*-xylene molecules are marked by orange and green thick line. Basing on the final Δρ map, it is likely that the disorder of xylene isomers is more complex.

1.3. Synthesis and characteristics of $[Cu_2(\mu\text{-ClPhtrz})_2(ClPhtrz)_2](ClO_4)_2$ (**1**)
1 was obtained by exposing any of above mentioned (in 1.3) **1-guest'** to the air, at ambient conditions or alternatively and faster at reduced pressure and/or at higher temperature**.** Formation of **1** was monitored by the PXRD experiments. Crystal data: $[C_{36}H_{28}Cl_4Cu_2N_{16}](ClO_4)_2$, M = 1152.52, monoclinic, $P2_1/c$, a = 7.093(2), b = 18.185(3), c = 18.270(3) Å, β = 90.40(3)º V = 2356.5(9) Å^3, Z = 2, D_c = 1.624 Mg m^{-3}, T = 293(2) K, R = 0.065, wR = 0.124 (473 reflections with $I > 2\sigma(I)$) for 170 variables, CCDC 949088



1 at RT



1 at 100 K

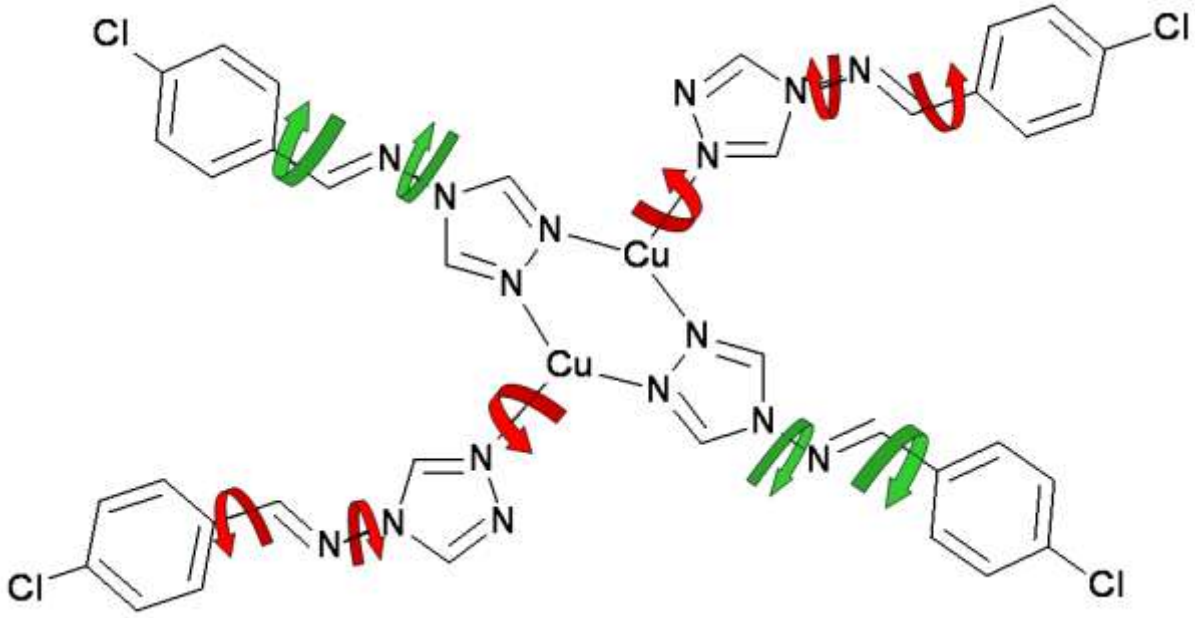
Fig. S9 Diffraction patterns of **1** and orientation of the unit cell at room temperature and 100 K viewed along *b**

2. Conformational analysis of 1-guest, 1-guest' and 1 (º);

Table. S1. Conformational analysis of **1-guest**, **1-guest'** and **1** (º).

	1-CH_3CN	1-CH_3OH	1-CCl_4	1-C_7H_8	1-*o*-C_8H_{10}		1-*m*-C_8H_{10}	1-*p*- C_8H_{10}	1-$C_{10}H_8$	1
conf-1	0.76(17)	3.19(12)	1.2(5)	4.8(3)	5.87(14)	5.36(14)	5.03(9)	6.41(14)	3.7(6)	2.6(6)
conf-2	8.3(2)	7.29(15)	7.8(6)	4.6(4)	3.12(18)	4.40(18)	6.88(10)	5.93(16)	7.7(1.0)	13.2(6)
conf-3	2.2(3)	0.68(17)	1.9(7)	1.2(4)	1.71(16)	0.92(17)	0.79(11)	1.54(14)	1.7(9)	2.9(6)
conf-4	22.00(15)	23.17(10)	17.5(4)	19.7(2)	12.84(12)	23.03(10)	25.79(7)	14.86(12)	26.3(4)	11.8(5)
conf-5	5.2(3)	1.75(20)	2.2(8)	5.6(4)	6.99(16)	2.59(18)	2.04(13)	8.00(13)	3.4(1.0)	7.8(6)
conf-6	0.6(3)	1.04(18)	2.8(8)	1.3(4)	0.41(18)	1.18(18)	1.91(11)	0.75(15)	1.7(9)	4.4(4)
Cu...Cu	3.508	3.5168(7)	3.545(3)	3.4468(17)	3.5264 (0.0007)		3.5149(6)	3.4950(8)	3.502(3)	3.469(4)

conf-1 = interplanar angle between plane of four bridging N atoms and plane of bridging triazole ring,
conf-2 = interplanar angle between plane of bridging triazole ring and the N4 C1 C2 plane;
conf-3 = interplanar angle in bridging ligand between the N4 C1 C2 and phenyl ring plane;
conf-4 = interplanar angle between plane of four bridging N atoms and plane of triazole ring of monodentately coordinated ligand;
conf-5 = interplanar angle in monodentately coordinated ligand between plane of triazole ring and the N14 C11 C12 plane;
conf-6 = interplanar angle in monodentately coordinated ligand between the N14 C11 C12 and phenyl ring plane.



3. Intermolecular interactions in 1, 1-guest and 1-guest'.

Table. S2. Distances of Cu(I)...Cl^b (Cl atom of bridging ligand) and Cu(I)...Cl^m (Cl atom of monodentately coodridinated ligand) and Cl^m...Cl^m contacts in **1-guest, 1-guest'** and **1** (Å).

	Cu(I)...Cl^b(1)	Cu(I)...Cl^m(2)	Cl^m...Cl^m(3)
1-CH_3CN	3.1291(12)	3.2415(11)	3.1794(18)
1-CH_3OH	3.2062(12)	3.1602(13)	3.2065(13)
1-CCl_4	3.139(4)	3.173(4)	3.179(6)
1-C_7H_8	3.4538(20)	3.0882(19)	3.206(3)
1-*o*-C_8H_{10}	3.4792(13)	3.1568(13)	3.2984(16)
	3.6994(13)	3.1015(13)	3.5779(16)
1-*m*-C_8H_{10}	3.4300(11)	3.1267(11)	3.2665(10)
1-*p*-C_8H_{10}	3.5481(14)	3.1396(13)	3.2420 (15)
1-$C_{10}H_8$	3.336(4)	3.148(4)	3.332(7)
1	5.345(6)	3.744(4)	4.315(10)

1-CH_3CN (1) -x, 0.5+y, 0.5-z; (2) x, 1.5-y, 0.5+z; (3) -x+1, 2-y, -z;

1-CH_3OH (1) x, 1.5-y, 0.5+z, (2) x, 1.5-y, -0.5+z; (3) -1-x, 2-y, 2-z;

1-CCl_4 (1) -x+1, 0.5+y, 0.5-z; (2) x, 1.5-y, -0.5+z; (3) -x, 2-y, 1-z;

1-C_7H_8 (1) -x, -0.5+y, 0.5-z; (2) x, 0.5-y, 0.5+z; (3) -x+1, -y, -z;

1-*o*-C_8H_{10} (1a) x, 0.5-y, 0.5+z and (1b) x, 1.5-y, -0.5+z; (2a) x, 0.5-y, -0.5+z and (2b) x, 1.5-y, 0.5+z; (3a) -x, -y, -z+1 and (3b) -x+1, -y+2, -z-1;

1-*m*-C_8H_{10} (1) -x+1, -0.5+y, 1.5-z; (2) x, 0.5-y, -0.5+z; (3) -x, -y, -z+2;

1-*p*- C_8H_{10} (1) -x+1, -0.5+y, 0.5-z; (2) x, 1.5-y, -0.5+z; (3) -x, -y+1, -z+1;

1- $C_{10}H_8$ (1) -x+1, 0.5+y, 1.5-z; (2) x, 0.5-y, 0.5+z; (3) -x+2, -y+1, -z+1;

1 (1) x, 0.5-y, 0.5+z; (2) -x, -0.5+y, 1.5-z; (3) -x, 1-y, 2-z.