Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information File

Fascinating Interlocked Triacontanuclear Giant Nanocages

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Experimental Section

All reagents used in the present work were obtained commercial sources and were used without further purification unless otherwise stated. FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. C, H and N microanalyses were carried out with a 2400 Series-II CHN Analyzer; Perkin–Elmer, USA. Magnetic susceptibility measurements were collected using a Quantum Design MPMS-XL7 SQUID magnetometer and a Quantum Design PPMS VSM. Polycrystalline samples were embedded in Vaseline to prevent torqueing. All data were corrected for the diamagnetic contribution. Thermal analyses were carried out with a TA Instruments SDT Q600 under nitrogenous atmosphere with a flow rate of 100 mL/min and Powder X-ray diffraction patterns were collected on a Bruker D8 ADVANCE instrument. JEOL JEM 2010 high-resolution microscope instrument used for TEM experiment.

X-ray Crystallography: Diffraction intensities were collected on a Bruker D8 QUEST diffractometer with Mo-K_α radiation (λ = 0.71073Å) for the cages at 120 K. The structures were solved by SHELXT and all non-hydrogen atoms were refined by least-squares on F^2 utilizing the SHELXTL program suite and Olex2.[1] All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Crystallographic data are summarized in Table S3, and CIF files for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Deposition numbers are given in Table S3. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax 44 (1223)336 033; E-mail: deposit@ccdc.cam.ac.uk).

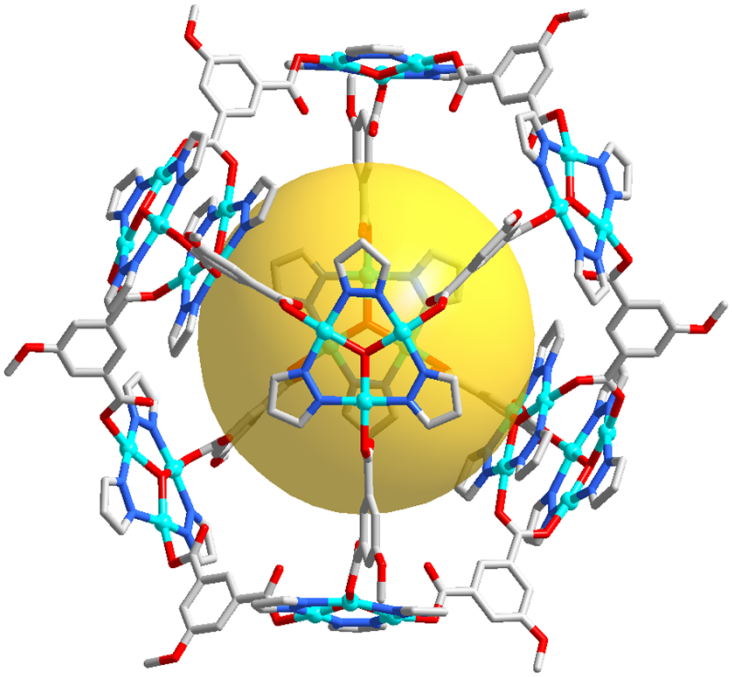

Fig. S1. Molecular structure of compound **MeO-Cu$_{30}$** showing hollow spherical metallocage resulted from joining Cluster-I and Cluster-II with 5-methoxy isophthalic acid.

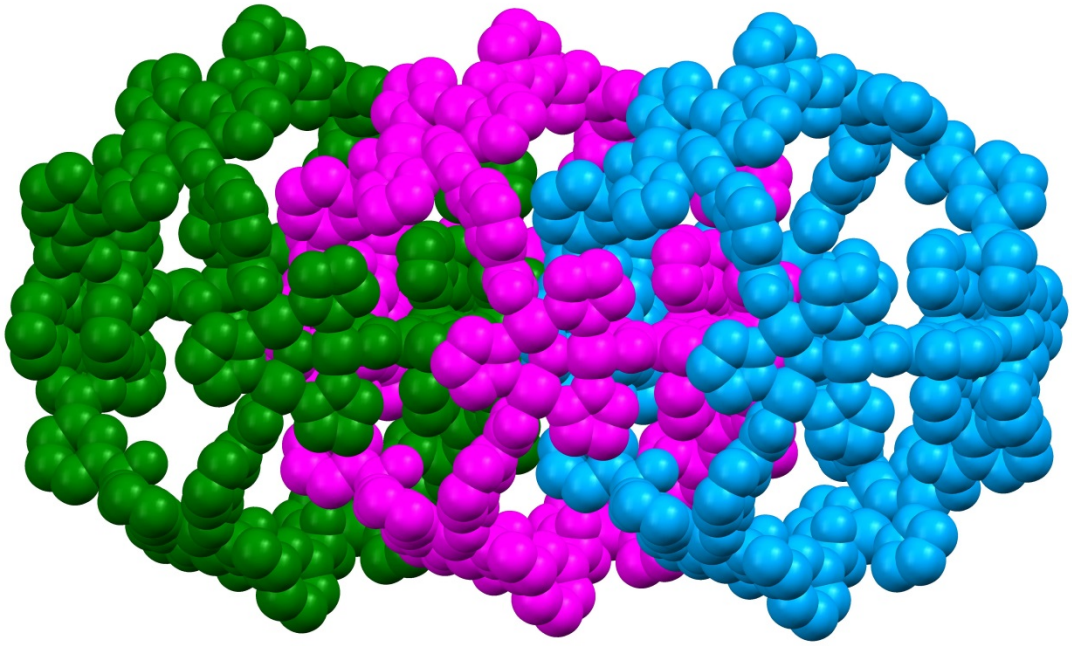

Fig. S2. A space-filled representation of three-fold interpenetrated metallocage.

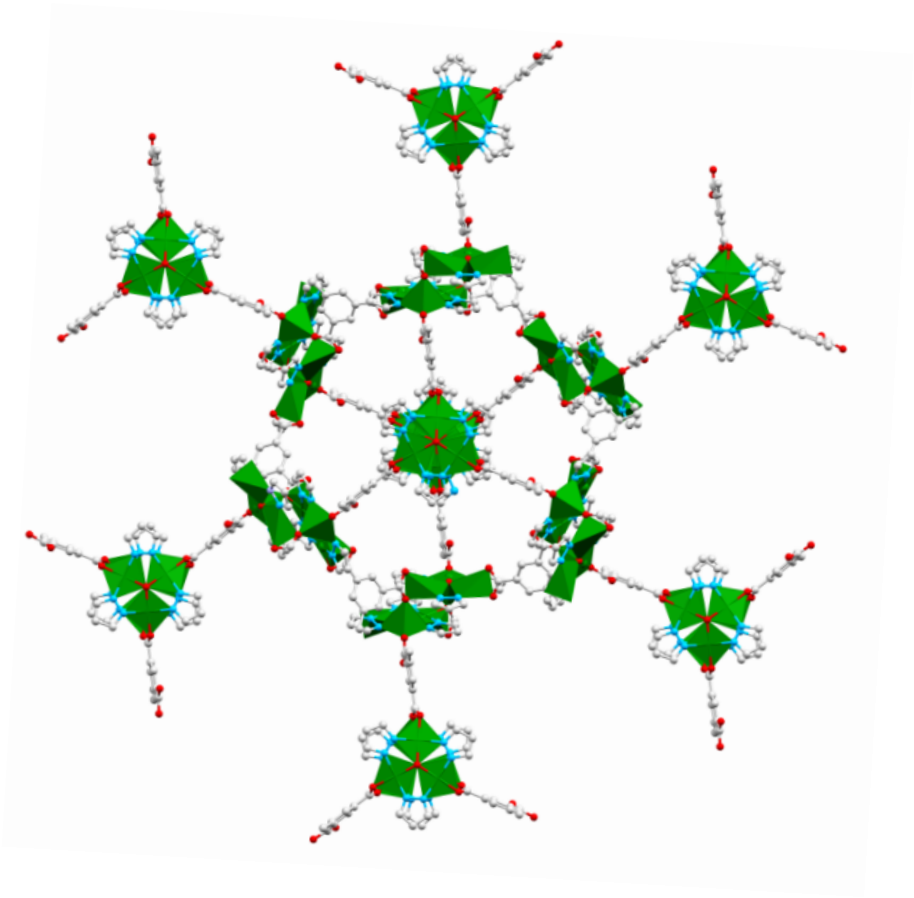

Fig. S3. Crystal structure of compound Me-Cu30 showing the polymeric nature and expansion of Cluster-Is via pi-pi stacking between the pyrazole moieties and metal-metal interaction.

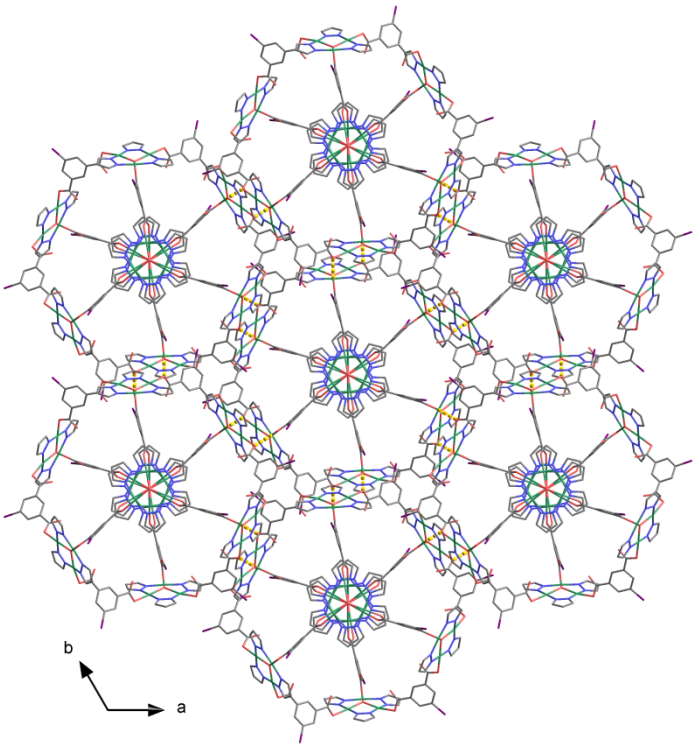

Fig. S4. Extended network of **Br-Cu$_{30}$**

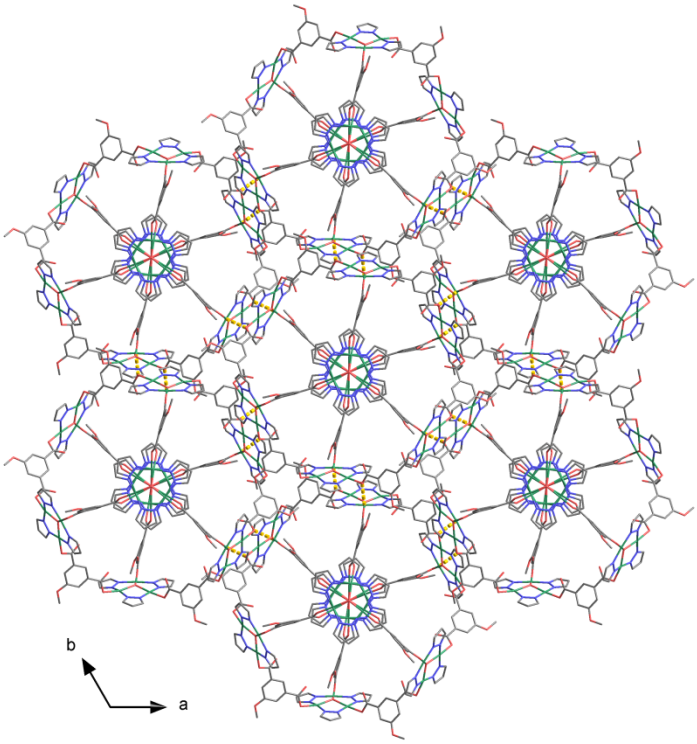

Fig. S5. Extended network of **MeO-Cu$_{30}$**

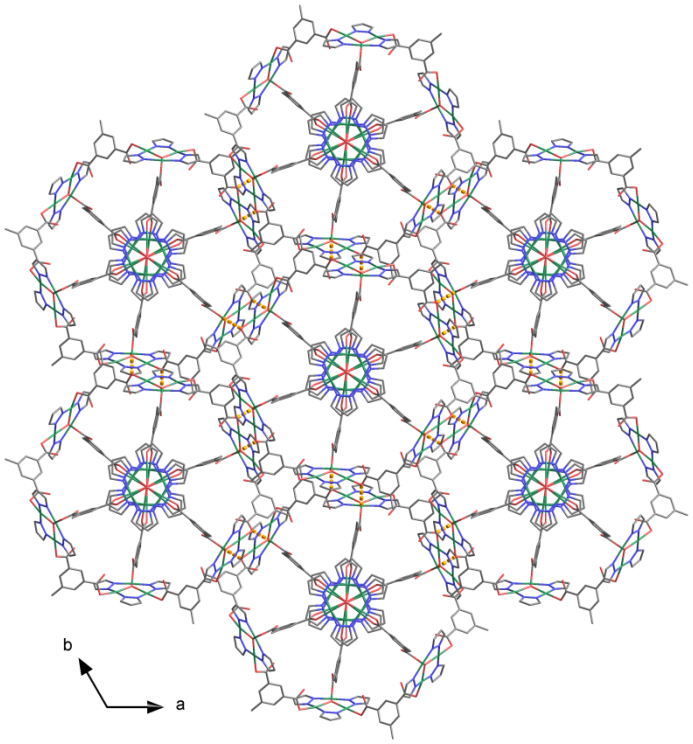

Fig. S6. Extended network of **Me-Cu$_{30}$**

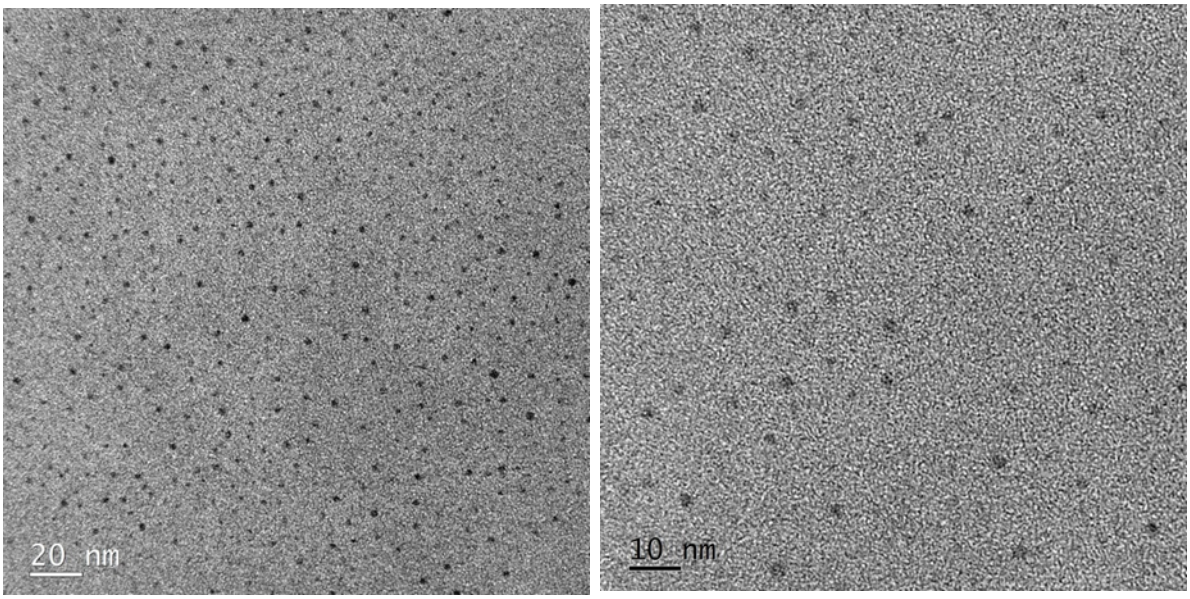

Fig. S7. HRTEM images showing the discretely existing nanocage of Br-Cu30.

The above studies unequivocally confirm the nanoscale-dimensions of metallocages with detail structural information at the molecular level. The obvious question then arose, do these metallocages of nano-dimensions are nanodimensional? Do above molecular cages exist in nano-dimension? Do they qualify as nanomaterials? It was gratifying to note that the answers are affirmative with corroborating morphological data from high resolution

transmission electron microscopy (HRTEM). In order to tackle above questions through microscopic studies were carried out for all three compounds. The sample was prepared by sonicating the nanocage in methanol for 8 hours. It was then carefully drop casted on a carbon coated copper grid (Cu, 300 mesh) and left overnight for drying up. TEM images provided visualization of the nanocage displaying both uniform size and the shapes of the dispersed molecule. The measured diameter are in the range of 3.2-3.4 nm which are well agreement with the size shown in crystallographic structure's outer diameter.

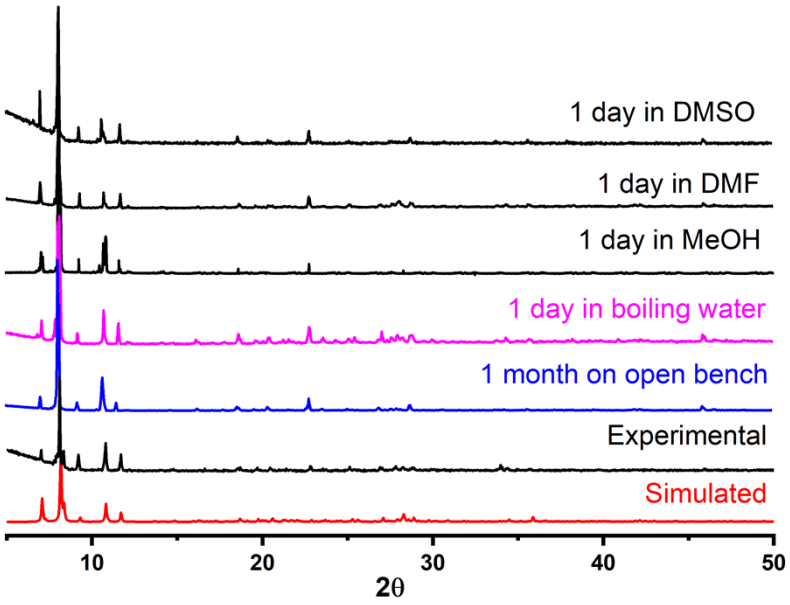

Fig. S8: PXRD patterns of **Br-Cu$_{30}$** after treatment under different condition.

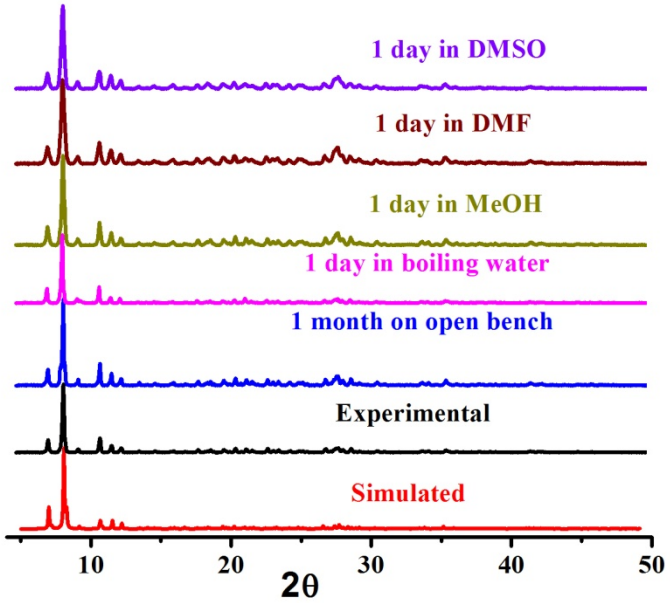

Fig. S9: PXRD patterns of **MeO-Cu$_{30}$** after treatment under different condition.

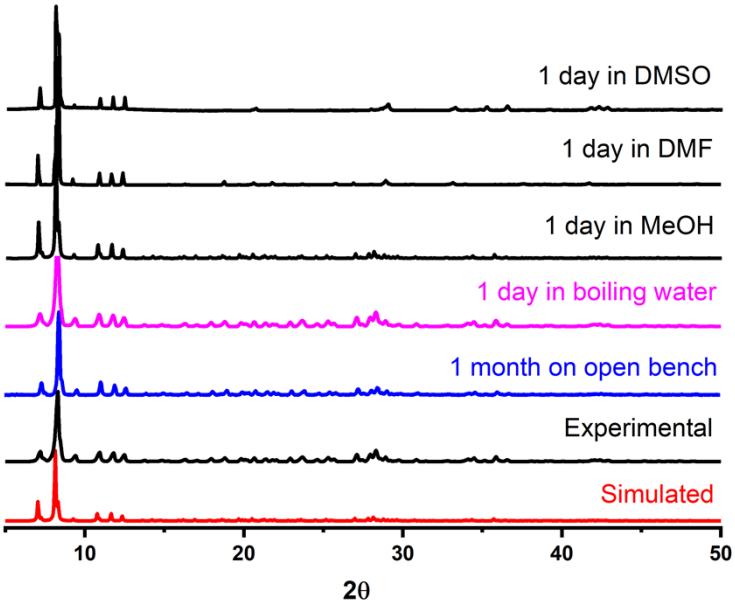

Fig. S10: PXRD patterns of **Me-Cu$_{30}$** after treatment under different condition.

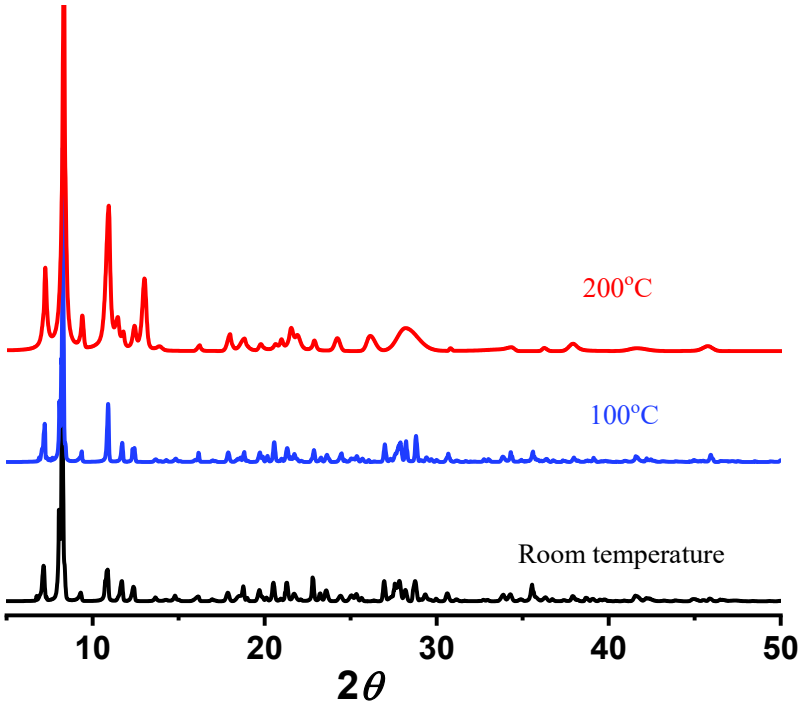

Fig. S11: PXRD patterns of **MeO-Cu$_{30}$** at different temperature.

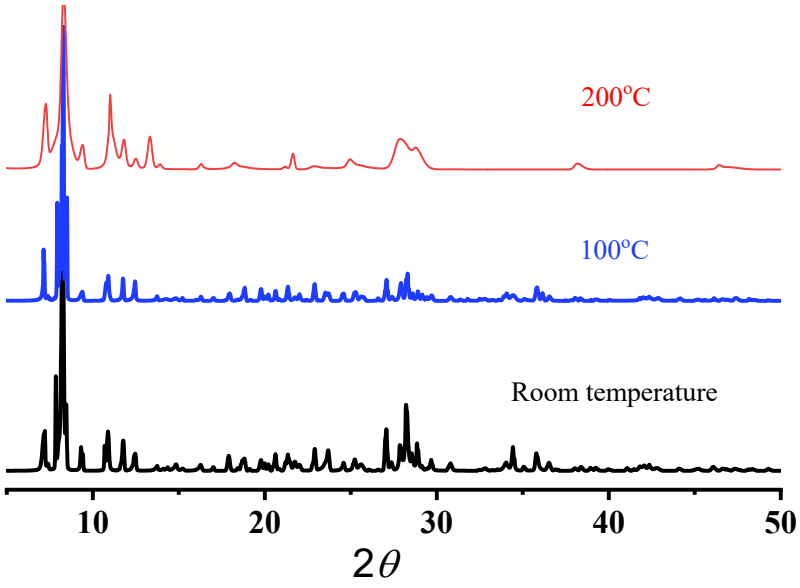

Fig. S12: PXRD patterns of **Me-Cu$_{30}$** at different temperature.

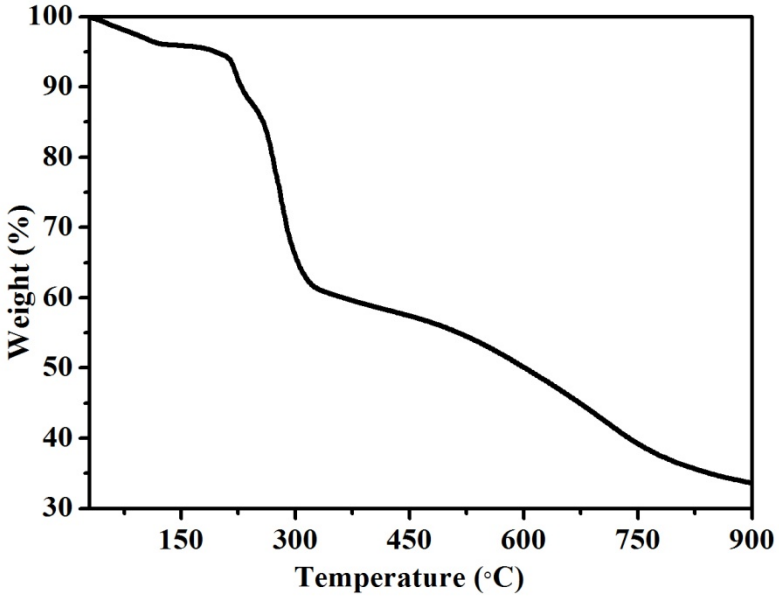

Fig. S13: TGA plots of **Br-Cu$_{30}$** under N_2 atmosphere.

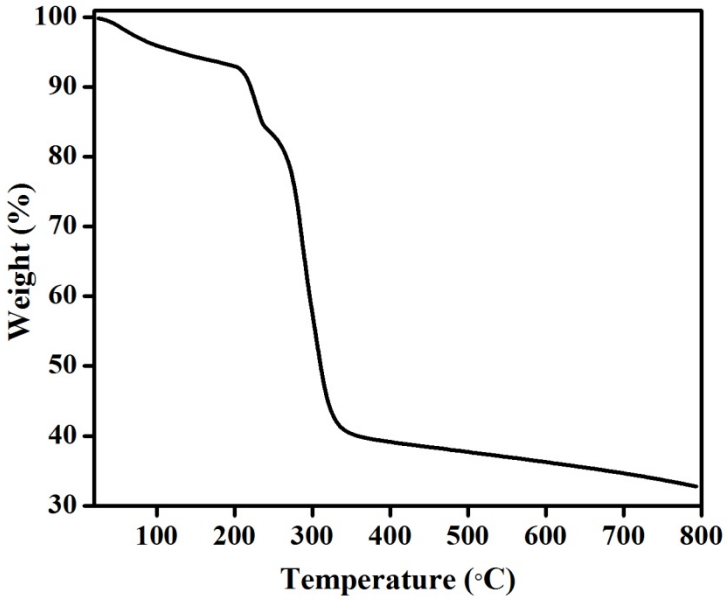

Fig. S14: TGA plots of **MeO-Cu$_{30}$**under N_2 atmosphere.

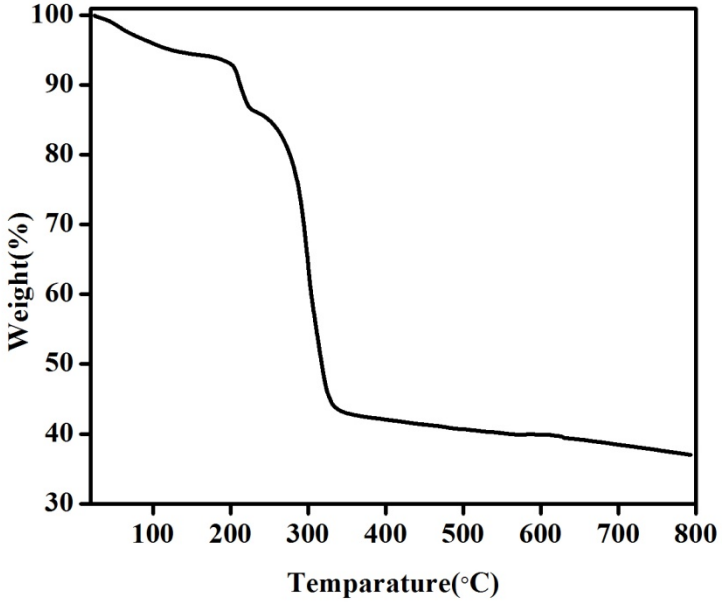

Fig. S15: TGA plots of **Me-Cu$_{30}$**under N_2 atmosphere.

The thermogravimetric analyses of three compounds were performed in platinum crucible at a rate of 10ºC per minute under nitrogenous atmosphere within the range of 25º-800ºC. The TGA curve revealed that the framework is stable over 250 °C which signify that our nanocages are highly stable and can be useful for further applications at high temperature. Furthermore, the chemical stability of all the cages was determined by PXRD when it was kept in open air and in water for one month. The cages were stable to other various organic solvents like methanol, dimethyl formamide, dimethyl sulphoxide etc. which are shown in figure8. The PXRD pattern of these cages was similar with the simulated pattern which confirms excellent chemical stability in these solvents. The thermal and chemical

stability may be arising due to the interpenetration between the cage and strong interaction between the adjacent CuII centres (Cu....Cu separation 3.4 Å) bridged by pyrazole moiety. To the best of our knowledge, this is the first example where pyrazole based Cu30nanocages with two types of inorganic cluster motif showed remarkable such kind of high thermal and chemical stability

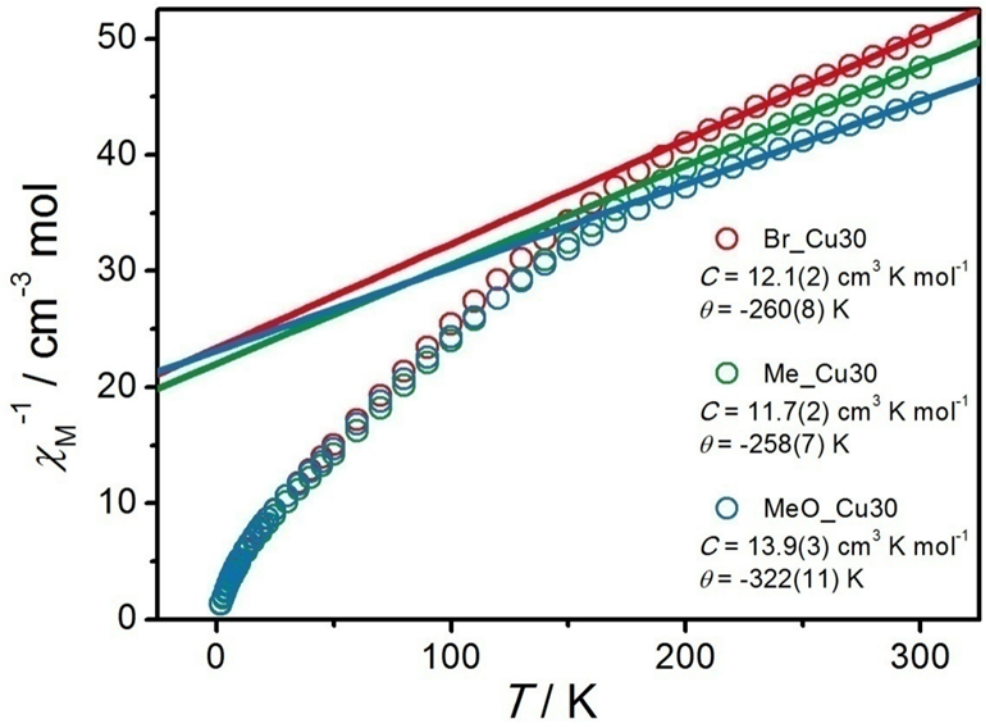

Fig. S16: Curie-Weiss fitting for **Br-Cu$_{30}$**, **MeO-Cu$_{30}$** and **Me-Cu$_{30}$**.

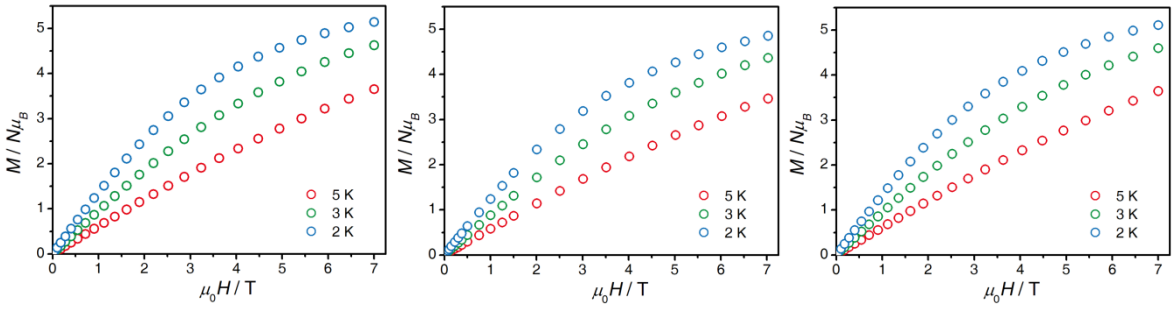

Fig. S17: Field dependence magnetization for **Br-Cu$_{30}$** (*left*), **MeO-Cu$_{30}$**(*middle*) and**Me-Cu$_{30}$**, (*right*).

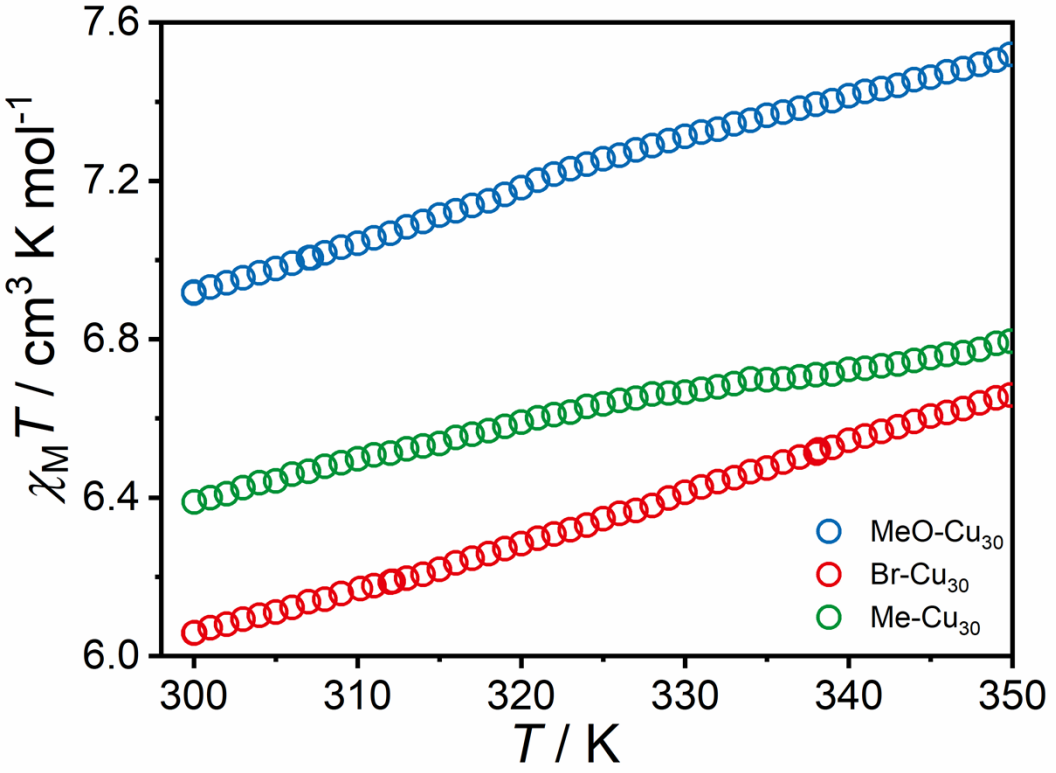

Fig. S18: Temperature dependence of $\chi_M T$ for Br-Cu_{30}, MeO-Cu_{30} and Me-Cu_{30} in the temperature range of 300-350K

Table S1: Selected bond lengths of cages

Br-Cu_{30}	**MeO-Cu_{30}**	**Me-Cu_{30}**
Cu_1....O_{1S} 1.996(3)	Cu_1....O_{1S}1.981(3)	Cu_1....O_{1S} 1.982(3)
Cu_1....O_{1A}1.967(4)	Cu_1....O_1 1.954(3)	Cu_1....$O_1$1.987(4)
Cu_1....N_{2B} 1.934(4)	Cu_1....N_{1A} 1.936(4)	Cu_1....$N_1$1.926(5)
Cu_1....N_{2A} 1.947(4)	Cu_1....N_{1B} 1.948(3)	Cu_1....N_{2B} 1.947(5)
Cu_2....O_{1S} 1.985(3)	Cu_2....O_{1S}1.990(3)	Cu_2....O_{1S}1.976(3)
Cu_2....O_1 1.992(4)	Cu_2....$O_3$1.992(3)	Cu_2....$O_3$1.965(4)
Cu_2....N_{1B}1.950(5)	Cu_2....$N_1$1.935(4)	Cu_2....N_2 1.934(5)
Cu_2....$N_1$1.931(5)	Cu_2....N_{2A} 1.930(4)	Cu_2....N_{1A}1.946(5)
Cu_3....O_{1S}1.969(3)	Cu_3....O_{1S} 2.003(3)	Cu_3....O_{1S}2.001(4)
Cu_3....$O_3$1.955(4)	Cu_3....O_{1A}1.972(3)	Cu_3....O_{1A} 1.969(4)
Cu_3....$N_2$1.936(5)	Cu_3....$N_2$1.937(3)	Cu_3....N_{2A}1.952(5)
Cu_3....N_{1A}1.951(4)	Cu_3....N_{2B}1.949(3)	Cu_3....N_{1B} 1.933(4)
Cu_4....O_{2S}1.9321(14)	Cu_4....O_{2S}1.9374(10)	Cu_4....O_{2S} 1.9337(13)
Cu_4....O_{4A}1.947(5)	Cu_4....O_{3A}1.954(3)	Cu_4....O_{4A}1.956(4)
Cu_4....N_{2D}1.921(6)	Cu_4....N_{1C}1.917(4)	Cu_4....N_{1C}1.925(6)
Cu_4....N_{1D}1.942(6)	Cu_4....N_{2C}1.948(4)	Cu_4....N_{2C}1.916(6)
Cu_5....O_{3S}1.9317(15)	Cu_5....O_{3S}1.9314(10)	Cu_5....O_{3S} 1.9369(12)
Cu_5....O_{3A}1.957(4)	Cu_5....O_{4A} 1.946(4)	Cu_5....O_{3A} 1.970(5)
Cu_5....N_{2C}1.931(5)	Cu_5....N_{1D}1.945(6)	Cu_5....N_{1D} 1.886(6)
Cu_5....N_{1C}1.929(5)	Cu_5....N_{2D} 1.897(5)	Cu_5....N_{2D} 1.974(7)

Table S2: Selected bond angles of cages

Br-Cu$_{30}$	**MeO-Cu$_{30}$**	**Me-Cu$_{30}$**
O_{1A}...Cu_1...O_{1S}166.09(15)	O_1...Cu_1...O_{1S}174.90(13)	O_{1S}...Cu_1...O_1 169.25(15)
N_{2B}...Cu_1...O_{1S}88.46(16)	N_{1A}...Cu_1...O_{1S} 89.82(13)	N_1...Cu_1...O_{1S}89.86(17)
N_{2B}...Cu_1...O_{1A} 92.59(18)	N_{1A}...Cu_1...$O_1$91.20(14)	N_1...Cu_1...$O_1$92.39(18)
N_{2B}...Cu_1...N_{2A}175.56(19)	N_{1A}...Cu_1...N_{1B}175.44(15)	N_1...Cu_1...N_{2B}173.2(2)
N_{2A}...Cu_1...O_{1S} 88.34(16)	N_{1B}...Cu_1...O_{1S}88.51(13)	N_{2B}...Cu_1...O_{1S}89.42(17)
N_{2A}...Cu_1...O_{1A} 91.25(17)	N_{1B}...Cu_1...$O_1$90.84(13)	N_{2B}...Cu_1...$O_1$89.56(18)
O_{1S}...Cu_2...$O_1$168.67(15)	O_{1S}...Cu_2...O_3 164.61(12)	O_3...Cu_2...O_{1S}178.57(15)
N_{1B}...Cu_2...O_{1S}89.49(16)	N_1...Cu_2...O_{1S}89.80(13)	N_2...Cu_2...O_{1S}89.71(17)
N_{1B}...Cu_2...$O_1$89.85(17)	N_1...Cu_2...$O_3$90.14(13)	N_2...Cu_2...$O_3$91.14(18)
N_1...Cu_2...O_{1S}89.81(17)	N_{2A}...Cu_2...O_{1S}90.09(13)	N_2...Cu_2...N_{1A}177.9(2)
N_1...Cu_2...$O_1$91.99(17)	N_{2A}...Cu_2...$O_3$92.96(13)	N_{1A}...Cu_2...O_{1S}88.51(17)
N_1...Cu_2...N_{1B}174.1(2)	N_{2A}...Cu_2...$N_1$168.66(16)	N_{1A}...Cu_2...$O_3$90.66(18)
O_3...Cu_3...O_{1S}178.33(15)	O_{1A}...Cu_3...O_{1S}166.49(12)	O_{1A}...Cu_3...O_{1S}165.29(15)
N_2...Cu_3...O_{1S}89.76(16)	N_2...Cu_3...O_{1S}88.68(13)	N_{2A}...Cu_3...O_{1S} 87.99(17)
N_2...Cu_3...$O_3$91.08(18)	N_2...Cu_3...O_{1A}92.49(14)	N_{2A}...Cu_3...O_{1A}90.89(18)
N_2...Cu_3...N_{1A}177.76(18)	N_2...Cu_3...N_{2B}174.96(15)	N_{1B}...Cu_3...O_{1S}88.29(17)
N_{1A}...Cu_3...O_{1S}88.47(16)	N_{2B}...Cu_3...O_{1S}87.98(12)	N_{1B}...Cu_3...O_{1A}93.30(18)
N_{1A}...Cu_3...$O_3$90.72(17)	N_{2B}...Cu_3...O_{1A}91.64(14)	N_{1B}...Cu_3...N_{2A}175.59(19)
O_{2S}...Cu_4...O_{4A}176.5(2)	O_{2S}...Cu_4...O_{3A}176.24(16)	O_{2S}...Cu_4...O_{4A}175.0(2)
O_{2S}...Cu_4...N_{1D}88.89(18)	O_{2S}...Cu_4...N_{2C}88.81(11)	N_{1C}...Cu_4...O_{2S}89.06(19)
N_{2D}...Cu_4...O_{2S} 89.35(19)	N_{1C}...Cu_4...O_{2S}89.24(12)	N_{1C}...Cu_4...O_{4A}90.3(3)
N_{2D}...Cu_4...O_{4A}91.7(3)	N_{1C}...Cu_4...O_{3A}91.08(16)	N_{2C}...Cu_4...O_{2S}89.33(19)
N_{2D}...Cu_4...N_{1D}174.8(2)	N_{1C}...Cu_4...N_{2C}174.73(15)	N_{2C}...Cu_4...O_{4A} 91.8(3)
N_{1D}...Cu_4...O_{4A}90.3(3)	N_{2C}...Cu_4...O_{3A}91.18(16)	N_{2C}...Cu_4...N_{1C}173.6(2)
O_{3S}...Cu_5...O_{3A}175.1(2)	O_{3S}...Cu_5...O_{4A}174.78(18)	O_{3S}...Cu_5...O_{3A}175.6(2)
N_{2C}...Cu_5...O_{3S}89.47(16)	O_{3S}...Cu_5...N_{1D}88.89(17)	O_{3S}...Cu_5...N_{2D}87.40(19)
N_{2C}...Cu_5...O_{3A}91.9(2)	N_{1D}...Cu_5...O_{4A}89.8(3)	O_{3A}...Cu_5...N_{2D} 91.3(3)
N_{1C}...Cu_5...O_{3S}89.15(16)	N_{2D}...Cu_5...O_{3S}89.50(17)	N_{1D}...Cu_5...O_{3S}89.96(19)
N_{1C}...Cu_5...O_{3A}90.0(2)	N_{2D}...Cu_5...O_{4A}92.4(3)	N_{1D}...Cu_5...O_{3A}91.7(3)
N_{1C}...Cu_5...N_{2C}173.7(2)	N_{2D}...Cu_5...N_{1D}173.52(17)	N_{1D}...Cu_5...N_{2D}174.2(2)

Table S3: Crystallographic data and refinement parameters for nanocages.

	Br-Cu$_{30}$	**MeO-Cu$_{30}$**	**Me-Cu$_{30}$**
Empirical formula	$C_{34.33}H_{38}Br_2Cu_5N_{10.67}O_{12.67}$	$C_{218}H_{263.99}Cu_{30}N_{64}O_{88}$	$C_{36.33}H_{44}Cu_5N_{10.67}O_{12.67}$
Formula weight	1280.27	7094.99	1150.52
Crystal system	Trigonal	Trigonal	Trigonal
Space group	*R*-3	*R*-3	*R*-3
a/Å	43.2076(11)	43.6103(11)	43.3455(13)
b/Å	43.2076(11)	43.6103(11)	43.3455(13)
c/Å	12.7945(4)	12.8640(3)	12.7232(4)
α/°	90	90	90
β/°	90	90	90
γ/°	120	120	120
V/Å^3	20685.9(12)	21187.7(9)	20702.1(11)
Z	18	3.00006	18
μ(Mo Kα)/mm^{-1}	4.086	2.296	2.345
Goodness-of-fit on F^2	1.058	1.032	1.035
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Reflections Collected	39468	32388	55327
Independent reflections	10529	10700	10600
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.0581, wR_2 = 0.1382	R_1 = 0.0506, wR_2 = 0.1225	R_1 = 0.0546, wR_2 = 0.1314
Final *R* indexes [all data]	R_1 = 0.0749, wR_2 = 0.1456	R_1 = 0.0660, wR_2 = 0.1302	R_1 = 0.0662, wR_2 = 0.1378
Largest diff. peak/hole/eÅ^{-3}	2.538/−2.452	2.341/−1.772	2.785/−2.100
CCDC no	2011020	2011018	2011019

References

1.a) G. M. Sheldrick, *ActaCrystallogr., Sect. C: Struct. Chem.,*2015, **71***,* 3; b) G. M. Sheldrick, *ActaCrystallogr., Sect. A: Found. Adv.*2015, **71***,* 3; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann*, J. Appl. Crystallogr*.2009, **42***,* 339.