Multifunctional Single-layered Vesicles Derived from Cu(II)-Metal-Organic-Polyhedra

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Electronic Supporting Information

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Experimental Section:

Materials and Physical measurements:

All the chemicals were commercially available and used without further purification. 1,3,5-tris(isonicotinamidomethyl)-2,4,6-trimethylbenzene (L1) and 1,3,5-tris(isonicotinamidomethyl)-2,4,6-triethylbenzene (L2) were synthesized by coupling of isonicotinoyl chloride with 1,3,5-trisamine-2,4,6-trimethylbenzene or 1,3,5-trisamine-2,4,6-triethylbenzene. The central scaffold 1,3,5-trisamine-2,4,6-trimethylbenzene and 1,3,5-trisamine-2,4,6-triethylbenzene were synthesized following a known procedure.[1] FT-IR spectra were obtained on a FT-IR instrument (FTIR-8300, Shimadzu). The elemental compositions of the purified compounds were confirmed by elemental analysis (Perkin Elmer Precisely, Series-II, CHNO/S Analyser-2400). TGA analyses were performed on a SDT Q Series 600 Universal VA.2E TA instrument. X-ray powder diffraction patterns were recorded on a Bruker AXS D8 Advance Powder (Cu Kα1 radiation, λ=1.5406 Å) X-ray diffractometer. TEM images were recorded using a JEOL instrument with 300 mesh copper TEM grid. Diameter of the vesicle from TEM images was measured using ImageJ software (version- 1.41o/Java 1.8.0_45). AFM images were taken with an NTMDT instrument, model no. AP-0100 in semi contact-mode. UV−Vis spectroscopic measurements were carried out on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a Peltier temperature controller. NMR spectra were recorded using 300 MHz spectrometer (Bruker Ultrasheild Plus- 300). Emission spectra were recorded with a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. Fluorescence images has been collected in light microscope (BX51, Olympus) equipped with a 100 W mercury lamp housing for an exciter and a excitation band filter covering wavelengths 420−440 nm. Dynamic light scattering experiments were executed using Malvern Particle Size Analyser (Model No. ZEN 3690 ZETASIZER NANO ZS 90 version 7.03). MTT assay were conducted using a multiplate ELISA reader (Varioskan Flash Elisa Reader, Thermo Fisher). Confocal microscopy was done in a C1 Nikon confocal microscopy. CD data were collected in a JASCO CD spectrometer (model-J815).

Synthesis of coordination polymers and metal-organic polyhedra:

$[\{Cu(L1)\cdot ClO_4\}\cdot 4DMF]_\alpha$ (CP1): CP1 was synthesized by layering a solution of ligand (40 mg, 0.0765 mmol) (L1) in DMF/ethanol (1:4, 15 ml) to an aqueous solution of $Cu(ClO_4)_2$ (28.3 mg, 0.0765 mmol) (3 ml).The resulting solution was kept for slow evaporation at room temperature. After four weeks well-formed block-shaped blue crystals were obtained. The crystals were washed with ethanol and characterized by elemental analysis, PXRD, and FT-IR. Yield: 25.99% (26 mg, 0.0198 mmol); elemental analysis calcd (%) for $C_{42}H_{58}CuClN_{10}O_{11}$: C 51.58, H 5.98, N 14.32; found: C 51.36, H 5.93, N 14.06; FT-IR (KBr pellet): $\tilde{\upsilon}$ =3380.98, 3357.84, 3110.97, 3074.32, 2960.53, 2923.88, 2854.45, 1643.24 (s), 1602.74, 1533.30 (s), 1425.30, 1369.37, 1290.29, 1201.57, 1145.64, 1110.92, 1087.78 (s), 1035.70, 970.13, 833.19, 796.55, 742.54, 702.04, 653.82, 626.82 cm^{-1}.

[{Cu(L1)·BF_4}·4DMF]$_\alpha$ (CP2): CP2 was synthesized by the similar procedure like CP1, except in place of $Cu(ClO_4)_2$, $Cu(BF_4)_2$ (18.15 mg, 0.0765 mmol) was used. After two weeks well-formed block-shaped blue crystals were obtained. The crystals were washed in ethanol and characterized by elemental analysis, PXRD, and FT-IR. Yield: 28.54% (28 mg, 0.022 mmol); elemental analysis calcd (%) for $C_{42}H_{58}CuBF_4N_{10}O_7$: C 52.26, H 6.06, N 14.51; found: C 52.36, H 5.93, N 14.06; FT-IR (KBr pellet): $\tilde{\upsilon}$ = 3736.01- 3127.12 (brs), 3058.46, 2962.83, 2915.43, 2846.77, 2463.46, 1964.90, 1650.24 (s), 1540.72 (s), 1492.5, 1424.66, 1349.47, 1287.55, 1226.06, 1061.77 (s), 850.09, 761.01, 692.35 cm^{-1}.

[{Cu(L1)·NO_3}·4DMF]$_\alpha$ (CP3): CP3 was synthesized by the similar procedure like CP1, except in place of $Cu(ClO_4)_2$, $Cu(NO_3)_2$ (18.5 mg, 0.0765 mmol) was used. After two weeks well-formed block-shaped blue crystals were obtained. The crystals were washed in ethanol and characterized by elemental analysis, PXRD, and FT-IR. Yield: 23.32% (22 mg, 0.018 mmol); elemental analysis calcd (%) for $C_{42}H_{58}CuN_{11}O_{10}$: C 53.63, H 6.22, N 16.38; found: C 54.06, H 6.43, N 16.06; FT-IR (KBr pellet): $\tilde{\upsilon}$ = 3411.84, 3263.33, 3055.03, 2968.24, 2923.88, 2854.45, 2426.28, 1764.75, 1643.24 (s), 1548.73 (s), 1492.80, 1450.37, 1382.87 (s), 1357.79, 1298.00, 1226.64, 1155.28, 1062.70, 1047.27, 1027.99, 850.55, 798.47, 759.90, 688.54 cm^{-1}.

[{$Cu_6(L2)_{12}$·Cl_6·6(H_2O)}·(NO_3)$_6$·8DMSO·90(H_2O)] (MOP1): MOP1 was synthesized by layering a solution of ligand (43 mg, 0.0765 mmol) (L2) in DMSO/acetonitrile (1:4, 15 ml) to an aqueous solution of $Cu(NO_3)_2$ (18.5 mg, 0.0765 mmol) (3 ml).The resulting solution was kept for slow evaporation at room temperature. After six weeks well-formed block-shaped blue crystals were obtained. The crystals were washed with acetonitrile and characterized by elemental analysis, PXRD, and FT-IR. Yield: 9.82% (42 mg, 0.007 mmol); elemental analysis calcd (%) for $C_{280}H_{528}Cu_6Cl_6N_{54}O_{146}S_8$: C 42.91, H 6.79, N 9.65; found: C 42.56, H 6.93, N 9.26; FT-IR (KBr pellet): $\tilde{\upsilon}$ = 3751.6- 3277.22 (brs), 3061.46,1656.23 (s), 1595.12 (s), 1532.25 (s), 1478.02, 1366.78 (s), 1295.55, 1153.34, 1052.22, 1029.29 (s), 953.43, 825.25, 700.11 cm^{-1}.

[{$Cu_6(L2)_{12}$·($Br)_6$}·($Br)_6$·8DMSO·90(H_2O)] (MOP2): MOP2 was synthesized by the similar procedure like MOP1, except in place of $Cu(NO_3)_2$, $CuBr_2$ (17.09 mg, 0.0765 mmol) was used. After two weeks well-formed block-shaped blue crystals were obtained. The crystals were washed in ethanol and characterized by elemental analysis, PXRD, and FT-IR. Yield: 12.05% (54 mg, 0.009 mmol); elemental analysis calcd (%) for $C_{280}H_{516}Cu_6Br_{12}N_{48}O_{122}S_8$: C 41.50, H 6.42, N 8.30; found: C 41.36, H 6.93, N 8.06; FT-IR (KBr pellet): $\tilde{\upsilon}$ = 3742.5- 3092.78 (brs), 3038.02, 2962.84, 2908.07, 2867.21, 2456.92, 1971.44, 1650.24 (s), 1526.83 (s), 1485.96, 1417.31, 1369.90, 1280.82, 1219.51, 1144.33, 1020.91(s), 945.72, 856.63, 754.47, 685.82 cm^{-1}.

Single crystal X-ray diffraction: Single crystal X-ray data were collected using Mo Kα (λ = 0.7107 Å) radiation on a SMART APEX- II diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution and refinement were carried out using the

software package of SMART APEX-II. All the structures were solved by direct methods and refined in a routine manner. For CP1-CP3 two of the three pyridyl rings and for CP1 and CP3 metal bound anions were found to be rotationally disordered over two positions (site occupancy factors (SOF) for CP1 - 0.482(7), 0.518(7); 0.446(8), 0.554(8) and for perchlorate anion 0.398(14), 0.602(14)), for CP2 - 0.555(9), 0.445(9) and for CP3 - 0.526(13), 0.474(13) and for nitrate anion 0.36(3), 0.64(3)).

In all the cases, non-hydrogen atoms were treated anisotropically except for the disordered atoms. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed at their idealized positions. Unaccounted electron densities preferably disordered solvent molecules were SQUEEZED out.

Crystallographic data for the structural analysis of compounds reported herein have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 1495331-1495335. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/deposit).

Table S1: Crystallographic parameter table.

Crystal parameters	CP1	CP2	CP3	MOP1	MOP2
CCDC No	1495331	1495332	1495333	1495334	1495335
empirical formula	$C_{42}H_{58}CuClN_{10}O_{11}$	$C_{42}H_{58}CuBF_4N_{10}O_7$	$C_{42}H_{58}CuN_{11}O_{10}$	$C_{280}H_{528}Cu_6Cl_6N_{54}O_{146}S_8$	$C_{280}H_{516}Cu_6Br_{12}N_{48}O_{122}S_8$
formula weight	977.96	965.32	940.52	7835.93	8101.67
crystal size/mm	0.36 × 0.24 × 0.16	0.32 × 0.20 × 0.14	0.26 × 0.16 × 0.10	0.42 × 0.38 × 0.26	0.39 × 0.36 × 0.24
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	*C*2/c	*C*2/c	*C*2/c	$P\bar{1}$	*C*2/c
a /Å	36.068(8)	35.729(3)	35.509(10)	24.331(3)	34.915(3)
b/Å	14.096(3)	13.9528(11)	14.304(4)	24.388(3)	33.412(3)
c /Å	16.023(4)	15.8889(13)	15.395(4)	24.415(3)	34.291(3)
$\alpha/^0$	90	90	90	118.745(2)	90
$\beta/^0$	109.397(7)	109.211(2)	108.369(19)	91.861(2)	90.352(4)
$\gamma/^0$	90	90	90	118.748(2)	90
volume/$Å^3$	7684(3)	7479.9(11)	7421(4)	10461(2)	40002(5)
Z	4	4	4	1	4
F(000)	2716.0	2652.0	2572.0	2910.0	11968.0
μ MoKα /mm^{-1}	0.414	0.362	0.354	0.392	1.560
temperature/K	100	100	100	120	120
R_{int}	0.0696	0.0732	0.1386	0.0600	0.0716
range of h, k, l	$-47 \le h \le 44$, $-18 \le k \le 18$,	$-37 \le h \le 37$, $-14 \le k$	$-38 \le h \le 38$, $-15 \le k \le 15$, -	$-27 \le h \le 27$, $-26 \le k \le 23$, -	$-30 \le h \le 30$, $-29 \le k \le 29$, $-30 \le l \le 30$

	-21 ≤ l ≤ 20	≤ 14, -16 ≤ l ≤ 16	16 ≤ l ≤ 15	27 ≤ l ≤ 19	
θmin/max/°	1.197/ 28.274	1.207/ 21.726	1.547/ 22.835	1.669/ 23.542	1.454/ 18.352
Reflections collected/unique	52099/ 9360	25737/ 4430	16405/ 4893	33387/ 17221	266496 / 14367
data/restraints/parameters	9360/0/499	4430/0/468	4893/0/469	17221/1/1714	14367/0/1569
goodness of fit on F^2	1.018	1.041	0.985	0.978	1.032
final R indices [I>2σ(I)]	R_1 = 0.0872, wR_2 = 0.2608	R_1 = 0.0819, wR_2 = 0.2313	R_1 = 0.0844, wR_2 = 0.2365	R_1 = 0.0823, wR_2 = 0.2204	R_1 = 0.0842, wR_2 = 0.2205
R indices (all data)	R_1 = 0.1320, wR_2 = 0.2833	R_1 = 0.1322, wR_2 = 0.2587	R_1 = 0.1559, wR_2 = 0.2962	R_1 = 0.1350, wR_2 = 0.2475	R_1 = 0.0991, wR_2 = 0.2350

ORTEP plots and Hydrogen Bonding parameters CP1 – CP3 and MOP1, MOP2:

CP1

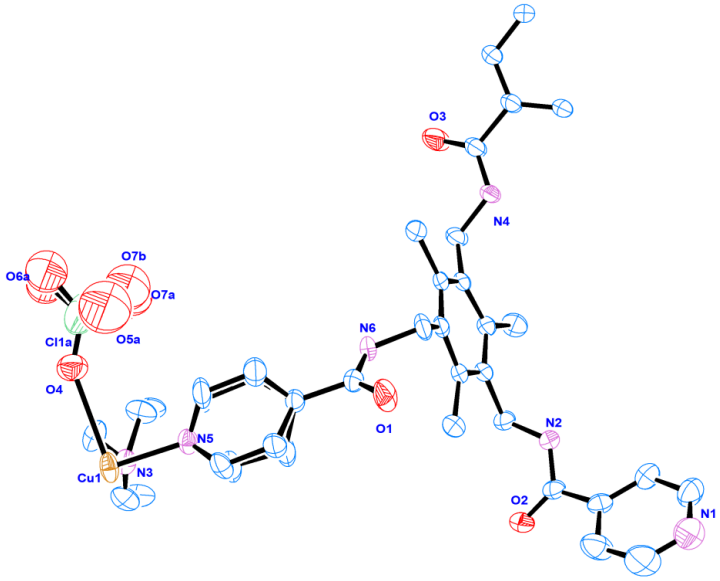


Figure S1. ORTEP plot of CP1 (30% ellipsoid probability). Few atoms are not marked to maintain the clarity.

Table S2: Hydrogen bonding parameters for CP1

D(D-H)	<DHA	d(D…A)	A	Symmetry operation		
C17-H17	155.09	3.412	N1	-x+3/2,	-y+1/2,	-z+2
C30A_a-H30A_a	132.78	3.581	Cl1A_a	x,	y,	z
C30A_a-H30A_a	163.17	3.12	O5A_a	x,	y,	z
C27A_a-H27A_a	129.74	3.533	Cl1A_a	x,	-y,	z+1/2
C28A_a-H28A_a	124.48	3.195	O4	-x+1,	-y,	-z
C28A_a-H28A_a	135.6	3.224	O6A_a	x,	-y,	z+1/2
C16-H16	142.44	3.353	O7A_a	x,	y,	z+1
N6-H6_a	163.85	2.949	O2	x,	-y,	z-1/2
N4-H4_a	165.72	3.12	O1	-x+3/2,	-y+1/2,	-z+1
C24A_a-H24A_a	158.19	3.052	O1	-x+3/2,	-y+1/2,	-z+1
C21A_a-H21A_a	112.66	3.059	O6A_a	-x+3/2,	-y+1/2,	-z
C22A_a-H22A_a	126.24	3.21	O4	x+1/2,	-y+1/2,	z+1/2
C22A_a-H22A_a	126.56	2.896	O6A_a	-x+3/2,	-y+1/2,	-z
C30B_b-H30B_b	158.81	3.092	O2	x,	-y,	z-1/2
C29B_b-H29B_b	148.26	3.341	O6B_b	x,	y,	z
C24B_b-H24B_b	141.59	3.63	Cl1B_b	x,	y,	z
C24B_b-H24B_b	117.25	3.128	O4	x,	y,	z
C24B_b-H24B_b	145.06	2.806	O6B_b	x,	y,	z

CP2

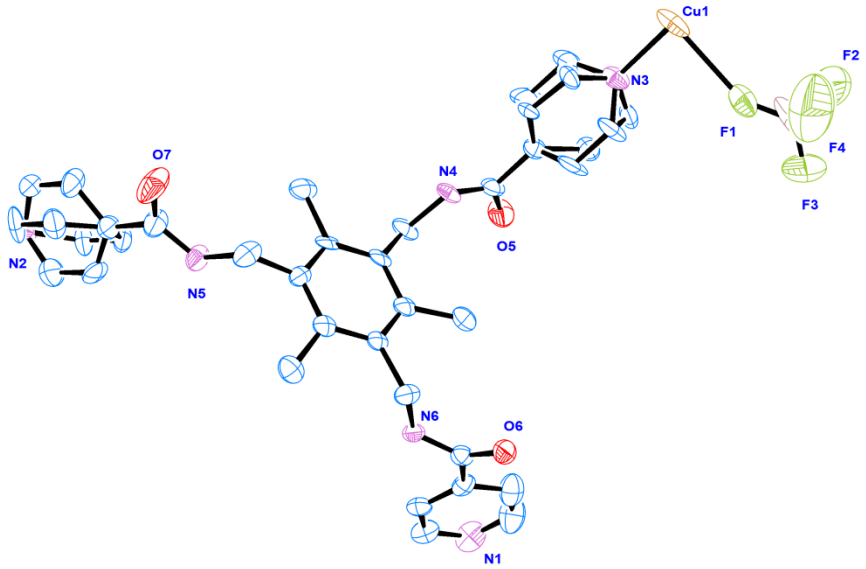


Figure S2. ORTEP plot of CP2 (30% ellipsoid probability). Few atoms are not marked to maintain the clarity.

Table S3: Hydrogen bonding parameters for CP2

D-H	<DHA	d(D..A)	A	Symmetry operation		
N4_a-H4_a	163.05	2.913	O6_a	x,	-y+1,	z+1/2
N5_a-H5_a	168.26	3.086	O5_a	-x+1/2,	-y+3/2,	-z+1
C29_a-H29_a	152.18	3.376	N1_a	-x+1/2,	-y+3/2,	-z
C18A_a-H18A_a	166.06	3.08	O6_a	x,	-y+1,	z+1/2
C17A_a-H17A_a	134.19	3.209	F2	-x+1,	-y+1,	-z+2
C23A_a-H23A_a	121.9	3.158	F1	-x+1/2,	y+1/2,	z+3/2
C23A_a-H23A_a	130.95	2.951	F3	x-1/2,	y+1/2,	z
C21A_a-H21A_a	151.09	3.058	O5_a	-x+1/2,	-y+3/2,	-z+1
C16A_a-H16A_a	116.38	3.148	F1	x,	y,	z
C23B_b-H23B_b	118.25	3.058	F1	x-1/2,	-y+3/2,	z-1/2
C23B_b-H23B_b	167.42	3.071	F2	x-1/2,	-y+3/2,	z-1/2
C15B_b-H15B_b	154.42	3.482	F2	-x+1,	y,	-z+3/2
C22B_b-H22B_b	124.05	3.213	F1	-x+1/2,	y+1/2,	-z+3/2
C22B_b-H22B_b	168.89	3.457	F4	-x+1/2,	y+1/2,	-z+3/2
C17B_b-H17B_b	151.88	2.961	F4	-x+1,	-y+1,	-z+2
C16B_b-H16B_b	132.69	2.677	F3	-x+1,	y,	-z+3/2

CP3

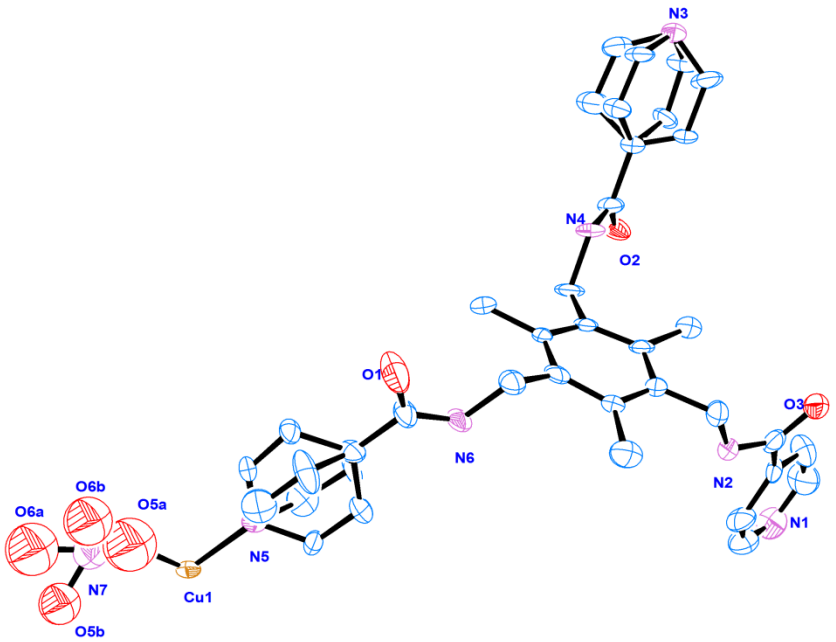


Figure S3. ORTEP plot of CP3 (30% ellipsoid probability). Few atoms are not marked to maintain the clarity.

Table S4: Hydrogen bonding parameters for CP3

D-H	<DHA	d(D..A)	A	Symmetry operation		
N6-H6	165.93	3.117	O2	-x+3/2,	-y+3/2,	-z+1
N4-H4	164.67	2.869	O3	x,	-y+1,	z+1/2
C16-H16	158.58	3.468	N1	-x+3/2,	-y+3/2,	-z
C17-H17	137.51	3.374	O6A_a	x+1/2,	-y+3/2,	z-1/2
C17-H17	147.02	3.259	O5B_b	x+1/2,	-y+3/2,	z-1/2
C24A_a-H24A_a	151.78	3.048	O3	x,	-y+1,	z+1/2
C30A_a-H30A_a	144.07	3.077	O2	-x+3/2,	-y+3/2,	-z+1
C30B_b-H30B_b	121.23	3.187	O4	x,	y,	z
C24B_b-H24B_b	130.61	3.307	O5B_b	x+1/2,	y-1/2,	z
C23B_b-H23B_b	123.37	3.038	O4	-x+3/2,	y-1/2,	-z+3/2
C22B_b-	125.18	3.251	O4	x+1/2,	-y+3/2,	z+1/2

H22B_b						
C22B_b-H22B_b	143.06	3.337	N7	x+1/2,	-y+3/2,	z+1/2
C27B_b-H27B_b	119.01	3.076	O4	-x+1,	-y+2,	-z+1
C27B_b-H27B_b	167.61	3.106	O5B_b	-x+1,	-y+2,	-z+1
C28A_a-H28A_a	124.23	3.213	O4	x,	y,	z

MOP1

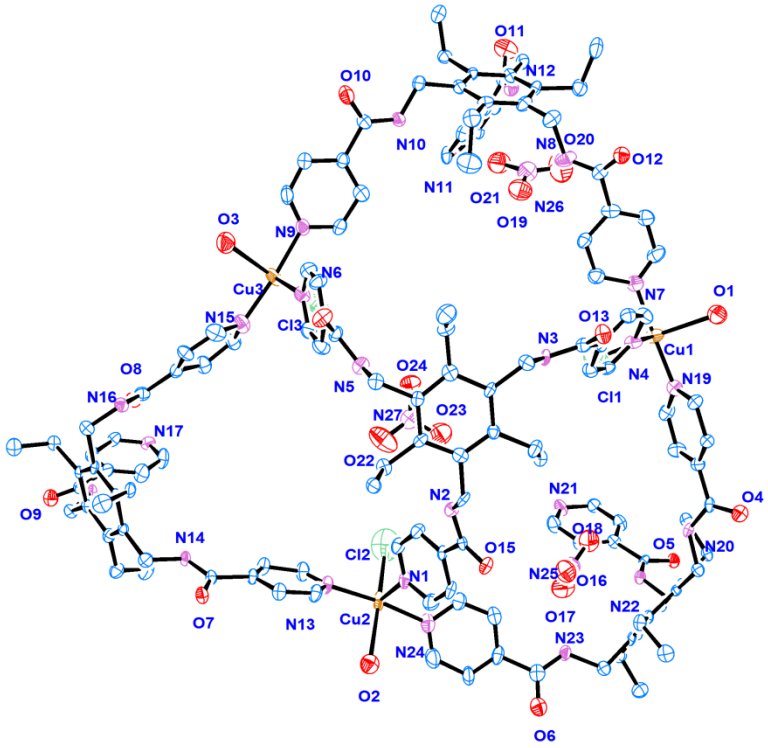


Figure S4. ORTEP plot of MOP1 (30% ellipsoid probability). Few atoms are not marked to maintain the clarity.

Table S5: Hydrogen bonding parameters for MOP1

D-H	<DHA	d(D..A)	A	Symmetry operation		
N2-H2	144.85	3.153	O23	x,	y,	z
N2-H2	160.71	3.484	O22	x,	y,	z
N22-H22	159.57	3.534	N25	x,	y,	z
N22-H22	142.9	3.086	O18	x,	y,	z
N22-H22	164.09	3.288	O17	x,	y,	z

N12-H12	167.22	2.929	O21	x,	y,	z
N23-H23	167.58	2.997	O16	x,	y,	z
N5-H5	149.66	2.945	O24	x,	y,	z
N5-H5	160.9	3.515	N27	x,	y,	z
N5-H5	151.41	3.405	O22	x,	y,	z
N8-H8	160.18	2.899	O19	x,	y,	z
C67-H67B	163.35	3.517	O15	-x+2,	-y+2,	-z+1
C79-H79	115.13	3.157	O1	x,	y,	z
C41-H41B	129.5	3.357	O7	-x+2,	-y+1,	-z+1
C53-H53	120.15	3.093	O1	x,	y,	z
C21-H21	173.47	3.408	O12	-x+1,	-y+2,	-z+2
C118-H118	116.24	3.316	Cl2	x,	y,	z
C20-H20A	118.53	3.086	O2	-x+1,	-y+1,	-z+1
C54-H54	162.91	3.35	O14	-x+2,	-y+2,	-z+2
C52-H52	113.92	3.273	Cl1	x,	y,	z
C101-H10C	135.79	3.274	O5	x,	y-1,	z
C18-H18A	127.37	3.195	O21	x,	y,	z
C80-H80	110.29	3.121	Cl1	x,	y,	z
C31-H31	122.3	3.209	O3	x,	y,	z
C84-H84	174.78	3.411	O17	x,	y,	z
C100-H10E	128.93	3.314	O15	-x+2,	-y+1,	-z+1
C7-H7A	113.47	3.116	O5	x,	y,	z+1
C27-H27	121.13	3.002	O11	-x+1,	-y+2,	-z+2
C57-H57	149.18	3.471	O23	x,	y,	z
C106-H106	121.5	3.16	Cl3	x,	y,	z
C32-H32	121.34	3.292	Cl3	x,	y,	z
C93-H93	165.54	3.162	O16	x,	y,	z
C92-H92	117.84	3.362	Cl2	x,	y,	z
C130-H130	113.08	3.137	N9	x,	y,	z
C113-H113	117	3.253	Cl1	-x+1,	-y+1,	-z+1
C25-H25	119.57	3.195	Cl1	x,	y,	z
C112-H112	110.42	3.108	O1	-x+1,	-y+1,	-z+1
C19-H19	116.13	3.311	Cl2	-x+1,	-y+1,	-z+1
C91-H91	112.54	3.091	O2	x,	y,	z

MOP2

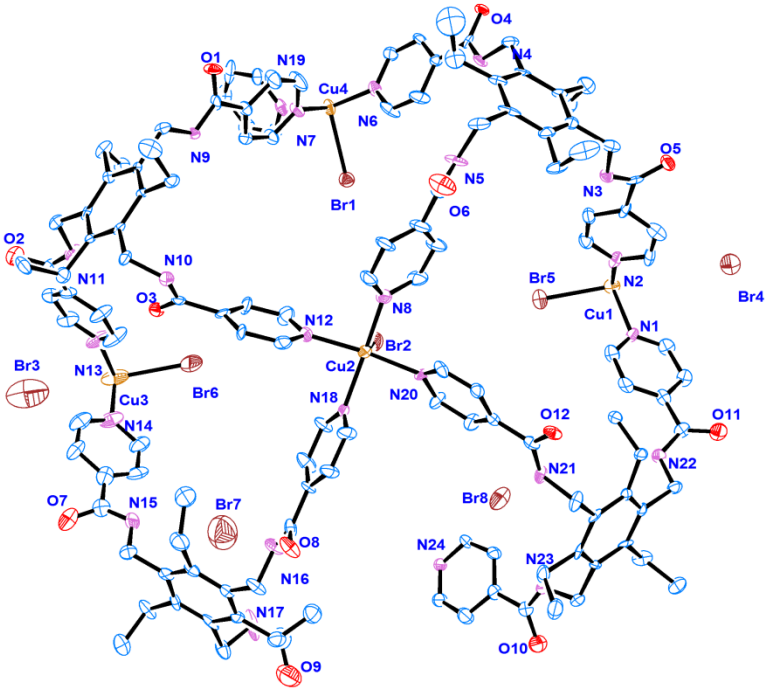


Figure S5. ORTEP plot of MOP2 (30% ellipsoid probability). Few atoms are not marked to maintain the clarity.

Table S6: Hydrogen bonding parameters for MOP2

D-H	<DHA	d(D..A)	A	Symmetry operation		
N21-HD	163.69	3.624	Br8	x,	y,	z
N23-HH	161.85	3.474	Br8	x,	y,	z
C87-HL	152.91	3.516	O2	-x+1/2,	y+1/2,	-z+1/2
C8-HM	116.41	3.19	O4	-x+1/2,	-y+1/2,	-z
N17-HP	167.22	3.373	Br7	x,	y,	z
C96-H0AA	118.46	3.632	Br8	x,	y,	z
C95-H1AA	125.17	3.589	Br1	-x+1,	y,	-z+1/2
C77-H7AA	159.01	3.44	O4	x,	-y+1,	z+1/2
C61-H9AA	127.07	3.505	Br5	x,	y,	z
C34-H0BA	116.48	3.659	Br1	x,	y,	z
C103-H8BA	139.99	3.117	O12	-x+1/2,	-y+1/2,	-z+1
C133-H3CA	123.84	3.658	Br5	x,	y,	z
C134-H4CA	132.21	3.716	Br4	x,	y,	z
C90-H7CA	168.99	3.697	Br8	x,	y,	z
C129-H8CA	127.74	3.581	Br1	x,	y,	z
C62-H0DA	138.2	3.757	Br4	x,	y,	z

C50-H3DA	143.39	3.441	O3	-x+1/2,	y+1/2,	-z+1/2
C9-H4DA	120.82	2.958	O12	-x+1/2,	y-1/2,	-z+1/2
C89-H8DA	122.52	3.531	Br2	x,	y,	z
N15-H4EA	138.94	3.724	Br7	x,	y,	z
C28-H8EA	117.93	3.506	Br3	x,	y,	z
C68-H3FA	120.61	3.704	Br2	x,	y,	z
C37-H5FA	120.23	3.605	Br1	x,	y,	z
C49-H5GA	122.05	3.191	O7	-x+1/2,	y+1/2,	-z+1/2
C22-H6GA	127.81	3.525	Br2	x,	y,	z
C128-H3HA	128.72	3.635	Br7	-x+1,	y,	-z-1/2
C126-H4HA	146.62	3.259	O7	x,	-y,	z-1/2
C121-H2JA	118.98	3.472	Br3	x,	y,	z
C123-H3JA	170.88	3.657	Br7	x,	y,	z
C122-H4JA	117.13	3.59	Br6	x,	y,	z
C29-H7JA	120.03	3.531	Br6	x,	y,	z
C24-H4KA	150.15	3.17	O5	-x+1/2,	y-1/2,	-z-1/2
C101-H5KA	124.1	3.596	Br2	x,	y,	z

SXRD analysis:

Crystal structure of [{Cu(L1)·(ClO_4)}·4DMF]$_\alpha$ CP1: SXRD data revealed that CP1 belongs to the centrosymmetric monoclinic space group *C*2/c. The asymmetric unit contained a 1,3,5-tris(isonicotinamidomethyl)-2,4,6-trimethylbenzene (**L1**), one perchlorate anion, one Cu^{II} metal ion located on a glide plane and smeared electron densities that were SQUEEZED out as it could not be modelled. The Cu^{II} metal center displayed an octahedral geometry wherein the equatorial sites were occupied by N atoms of **L1** whereas the axial sites were coordinated by O atoms of the anions. Two of the three pyridyl ring of the ligand **L1** was rotationally disordered over two positions (Refined Site Occupancy Factor (SOF) - 0.482(7), 0.518(7); 0.446(8), 0.554(8)). The anion was also found to be disordered over two positions (Refined SOF - 0.398(14), 0.602(14)). The structure could be best described as infinite 2D network wherein two pyridyl moieties were coordinated to the metal center and another one remains non-coordinated. The pyridyl arms were directed syn-syn-anti direction with respect to the trimethylbenzene platform. The non-coordinated pyridyl ring of one 2D layer stacked with the trimethylbenzene core of another 2D layer via π…π stacking that generates an overall 3D network structure. Parallel stacking of such 2D layer along c-direction generates an open channel in which smeared electron densities were located; indicating that they were loosely bound lattice occluded disordered solvent molecules. SQUEEZE calculations revealed that there were 205.5 electrons per asymmetric unit which might be attributed to ~4 DMF molecules. Elemental analysis further supports the analysis.

Crystal structure of [{Cu(L1)·(BF_4)}·4DMF]$_\alpha$ CP2: SXRD data revealed that CP2 belongs to the centrosymmetric monoclinic space group *C*2/c. The asymmetric unit contained a **L1**, one

tetrafluoroborate anion, one Cu^{II} metal ion located on a glide plane and smeared electron densities. The Cu^{II} metal center displayed an octahedral geometry wherein the equatorial sites were occupied by N atoms of **L1** whereas the axial sites were coordinated by F atoms of the anions. Two of the three pyridyl ring of the ligand **L1** was rotationally disordered over two positions (Refined Site Occupancy Factor (SOF) - 0.555(9), 0.445(9)). The crystal structure was found to be isomorphous with CP1, having identical crystal packing. Loosely bound lattice occluded disordered solvent molecules could not be modeled and therefore SQUEEZED out. SQUEEZE calculations revealed that there were 188.5 electrons per asymmetric unit which might be attributed to ~4 DMF molecules. Elemental analysis further supports the analysis.

Crystal structure of $[\{Cu(L1)\cdot(NO_3)\}\cdot 4DMF]_\alpha$ CP3: SXRD data revealed that CP3 belongs to the centrosymmetric monoclinic space group *C*2/c. The asymmetric unit contained **L1**, one nitrate anion, Cu^{II} metal ion located on a glide plane and smeared electron densities. The Cu^{II} metal center displayed an octahedral geometry wherein the equatorial sites were occupied by N atoms of **L1** whereas the axial sites were coordinated by O atoms of the anions. Two of the three pyridyl ring of the ligand **L1** was rotationally disordered over two positions (Refined Site Occupancy Factor (SOF) - 0.526(13), 0.474(13)). The anion was also found to be disordered over two positions (Refined SOF - 0.36(3), 0.64(3)). The crystal structure was found to be isomorphous with CP1, having identical crystal packing. Loosely bound lattice occluded disordered solvent molecules could not be modeled and therefore SQUEEZED out. SQUEEZE calculations revealed that there were 187.9 electrons per asymmetric unit which might be attributed to ~4 DMF molecules. Elemental analysis further supports the analysis.

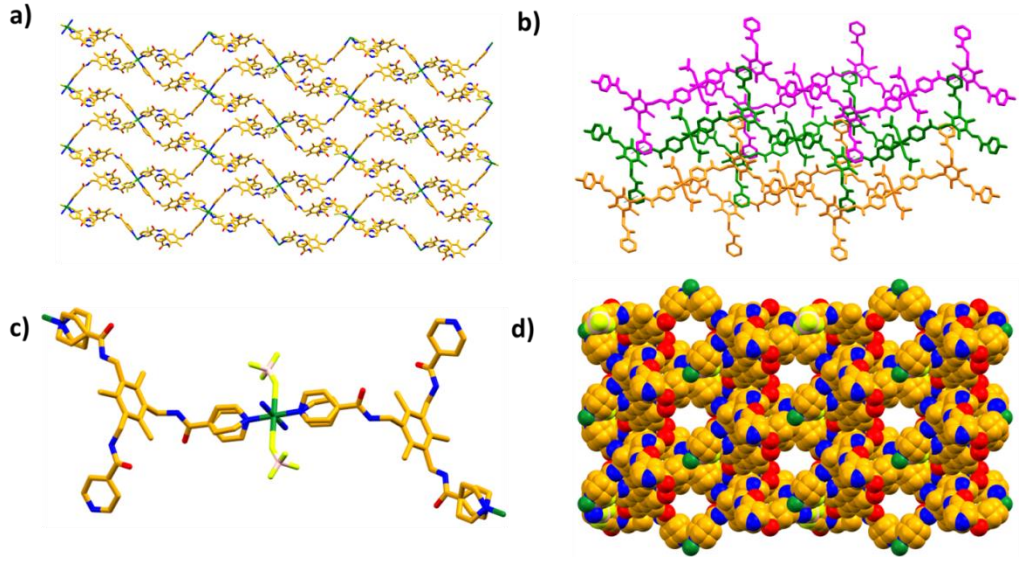


Figure S6. a) 2D sheet structure, b) Parallel π…π stacking of 2D layers, c) Representing unit showing *syn-syn-anti* conformation and d) Available open channel structure in CP2. CP1 and CP3 being isomorphous with CP2 displayed similar kind of structural features.

Crystal structure of [{$Cu_6(L2)_{12}\cdot Cl_6\cdot 6(H_2O)\}\cdot(NO_3)_6\cdot 8DMSO\cdot 90(H_2O)$] MOP1: SXRD data revealed that MOP1 belongs to the centrosymmetric triclinic space group $P\bar{1}$. The asymmetric unit contained four 1,3,5-tris(isonicotinamidomethyl)-2,4,6-triethylbenzene (**L2**), three Cu^{II} metal ion, three axially coordinated chloride, three axially coordinated water molecules and three nitrate anions - all located on a general position and smeared electron densities that were SQUEEZED out as it could not be modelled. The Cu^{II} metal center displayed an octahedral geometry wherein the equatorial sites were occupied by N atoms of **L2** whereas one of the axial sites was coordinated by water directed outside of the cage and other was coordinated by chloride directed inside the cage. Six nitrate anions were threaded within the cage via anion…π interaction (3.604-3.688 Å) with six triethylbenzene core. The structure could be best described as a discrete nanocage of dimension ~ 2.8 nm resembling a truncated octahedron and thus generate a large solvent accessible void within the structure wherein the smeared electron densities were located indicating the presence of loosely bound lattice occluded disordered solvent molecules. SQUEEZE calculations revealed that there were 1255 electrons per asymmetric unit which might be attributed to ~ 8 DMSO and 90 water molecules. Elemental analysis further supports the analysis.

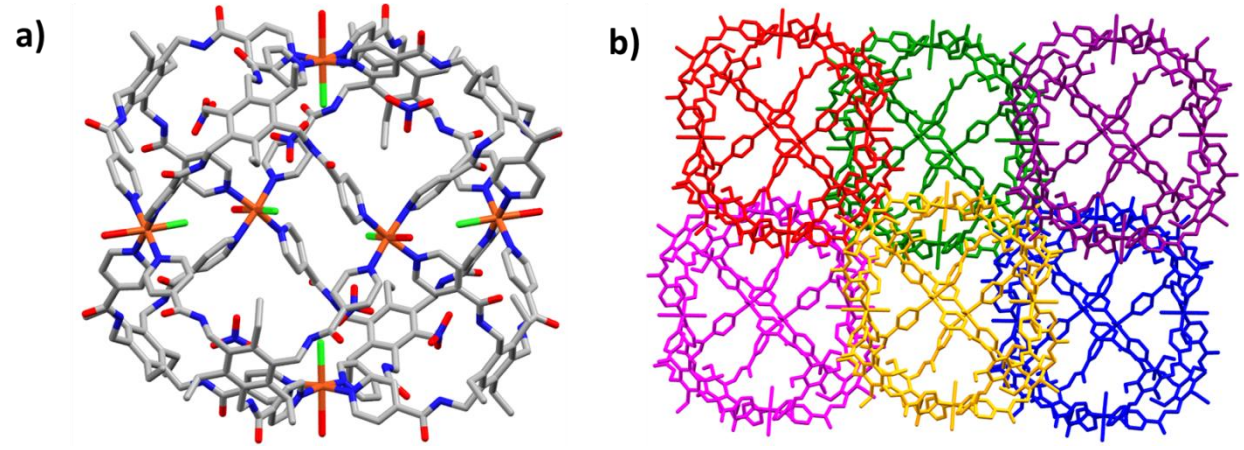


Figure S7. a) Single cage of MOP1, b) Packing of MOP1.

[{$Cu_6(L2)_{12}\cdot(Br)_6\}\cdot(Br)_6\cdot 8DMSO\cdot 90(H_2O)$] MOP2: SXRD data revealed that MOP2 belongs to the centrosymmetric monoclinic space group *C*2/c. The asymmetric unit contained four 1,3,5-tris(isonicotinamidomethyl)-2,4,6-triethylbenzene (**L2**), four Cu^{II} metal ion of which two were located on a two-fold symmetry axis, four axially coordinated bromide, four bromide anion and smeared electron densities that were SQUEEZED out as it could not be modelled. The Cu^{II} metal center displayed a square pyramidal geometry wherein the equatorial sites were occupied by N atoms of **L2** whereas the axial site was coordinated by bromide directed inside the cage. Two bromide anions were outside the cage and rest was threaded inside via anion…NH interaction (3.372-3.720 Å). The structure could be best described as a discrete nanocage of dimension ~ 2.8 nm resembling a truncated octahedron geometry and thus generate a large solvent accessible void within the structure wherein the smeared electron densities were located indicating the

presence of loosely bound lattice occluded disordered solvent molecules. SQUEEZE calculations revealed that there were 1396 electrons per asymmetric unit which might be attributed to ~ 8 DMSO and 90 water molecules. Elemental analysis further supports the analysis.

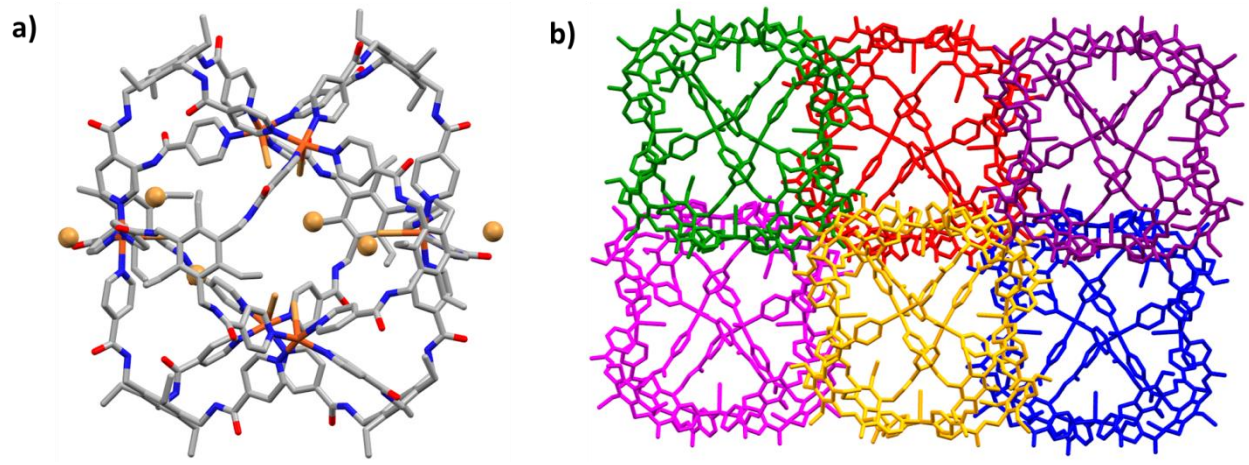


Figure S8. a) Single cage of MOP2, b) Packing of MOP2.

Calculation of available space within the nanocage in MOP1:
Distance between the centroids of two opposite π surface of the core triethylbenzene ring = 24.073 Å
van der Waals radii of π surface = 3.4 Å
Thus, the radius (r) of the imaginary sphere within the nanocage = [24.073 – 2(3.4)]/2 = 8.64 Å
So, the volume of the imaginary sphere = 4/3 πr^3 = 2700.28 $Å^3$
Volume occupied by six chlorine = 134.63 $Å^3$ (van der Waals radius of Cl = 1.75 Å)
Volume occupied by six nitrate = 347.94 $Å^3$ (van der Waals radius of N = 1.55, O = 1.55 Å)
So, available volume within the cage = (2700.28-134.63-347.94) = 2217.71 $Å^3$

Calculation of available pore volume in MOP2:
Distance between the centroids of two opposite π surface of core triethylbenzene ring = 24.28 Å
van der Waals radii of π surface = 3.4 Å
So, the radius of the imaginary sphere within the cage = [24.28 – 2(3.4)]/2 = 8.74 Å
So, the volume of the imaginary sphere = 2795.13 $Å^3$
Volume occupied by ten bromine = 265.08 $Å^3$ (van der Waals radius of Br = 1.85 Å)
So, available volume within the cage = (2795.13-265.08) = 2530.05 $Å^3$

TGA of Coordination Polymers and metal-organic polyhedra (CP1- CP3, MOP1 and MOP2):

CP1

Unit cell contents = 8 ligand L1 + 8 anion ClO_4^- + 4 Cu + 822 electrons squeezed from unit cell contributed by the solvent molecules.

Monoclinic *C*2/c space group, Z = 4

Therefore FW = Unitcell contents/Z

= 2 ligand L1 + 2 anion ClO_4^- + 1 Cu + 205.5 electrons
(~ 4 DMF molecules)

= 2×522.6 + 2×99.45 + 1×63.546 + 282

= 1045.2+ 198.9+ 63.546 + 282

= 1589.646

Weight loss for 4 DMF molecules

= 282/1589.646 X 100%

= 17.74 % Experimental Value (18.33 %)

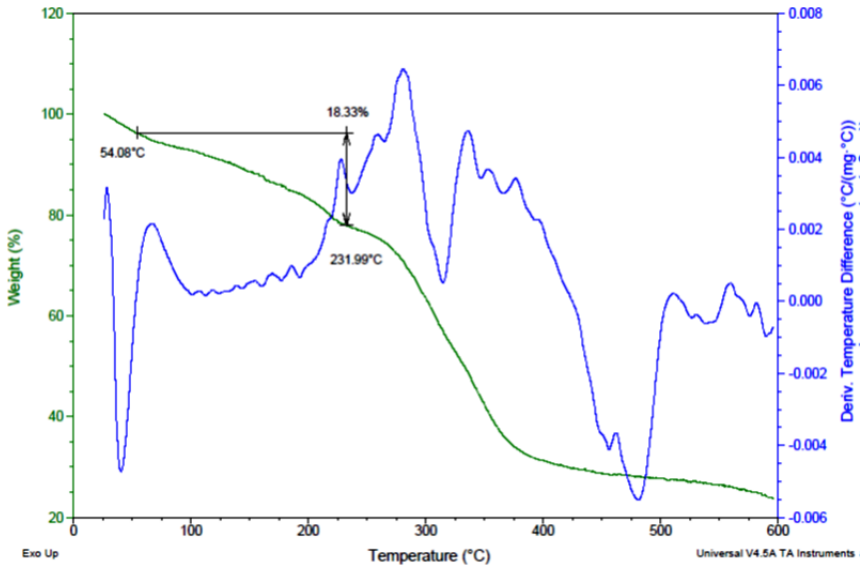


Figure S9: TGA profile of CP1.

CP2

Unit cell contents = 8 ligand L1 + 8 anion BF_4^- + 4 Cu + 754 electrons squeezed from unit cell contributed by the solvent molecules.

Monoclinic *C*2/c space group, Z = 4

Therefore FW = Unitcell contents/Z

= 2 ligand L1 + 2 anion BF_4^- + 1 Cu + 188.5 electrons
(~ 4 DMF molecules)

= 2×522.6 + 2×86.8 + 1×63.546 + 282

= 1045.2+ 173.6 + 63.546 + 282

= 1564.346

Weight loss for 4 DMF molecules

= 282/1564.346 X 100%

= 18.02 % Experimental Value (16.06 %)

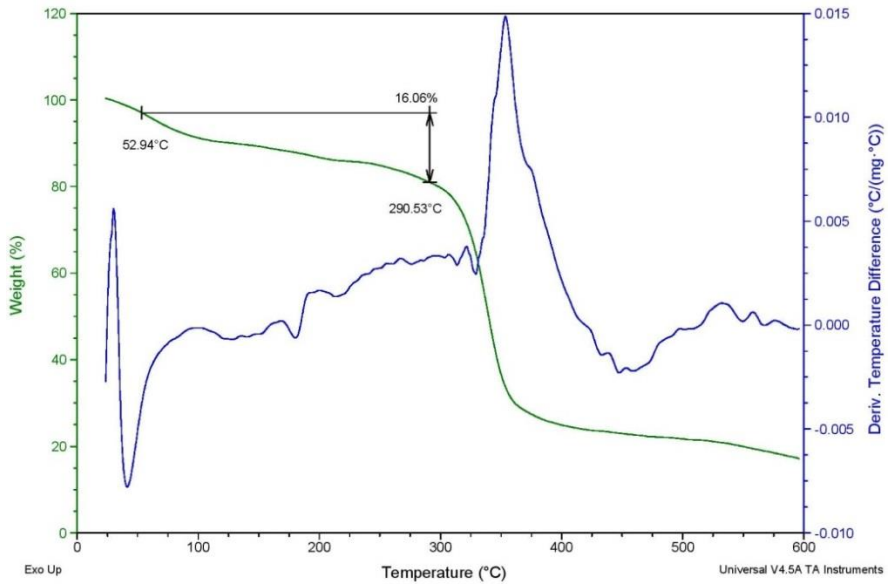


Figure S10: TGA profile of CP2.

CP3

Unit cell contents = 8 ligand L1 + 8 anion NO_3^- + 4 Cu + 751.8 electrons squeezed from unit cell contributed by the solvent molecules.

Monoclinic *C*2/c space group, Z = 4

Therefore FW = Unitcell contents/Z

= 2 ligand L1 + 2 anion NO_3^- + 1 Cu + 187.95 electrons

(~ 4 DMF molecules)

= 2×522.6 + 2×62.0 + 1×63.546 + 282

= 1045.2+ 124.0+ 63.546 + 365

= 1514.746

Weight loss for 4 DMF molecules

= 282/1514.746 X 100%

= 18.62 % Experimental Value (17.56 %)

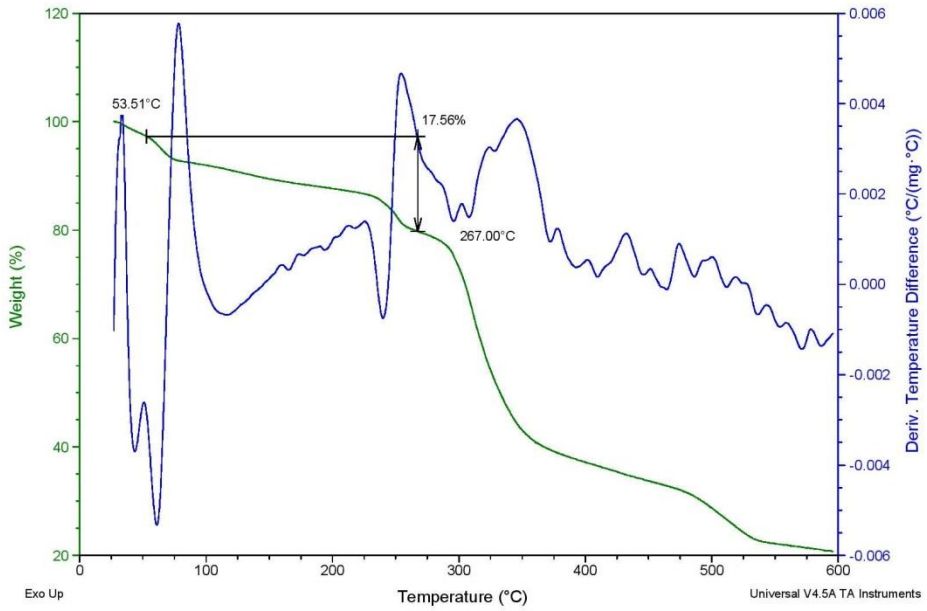


Figure S11: TGA profile of CP3.

MOP1

Unit cell contents = 8 ligand L2 + 48 anions Br^- + 6 Cu + 1255 electrons squeezed from unit cell contributed by the solvent molecules.

Monoclinic *P*-1 space group, Z = 1

Therefore FW = Unitcell contents/Z

= 8 ligand L1 + 6 anion Cl^- + 6 NO_3^- + 6 Cu + 6 coordinated water + 1255 electrons (~ 8 DMSO + 90 H_2O molecules)

= 8×564.6 + 6×35.5 + 6×62.0 + 6×63.546 + 108.06 + 2244.8

= 4516.8+ 213+ 372 + 381.276 + 108.06 + 2244.8

= 7835.936

Weight loss for 8 DMSO + 96 H_2O molecules

= 2352.86/7835.936 X 100%

= 30.02 % Experimental Value (28.80 %)

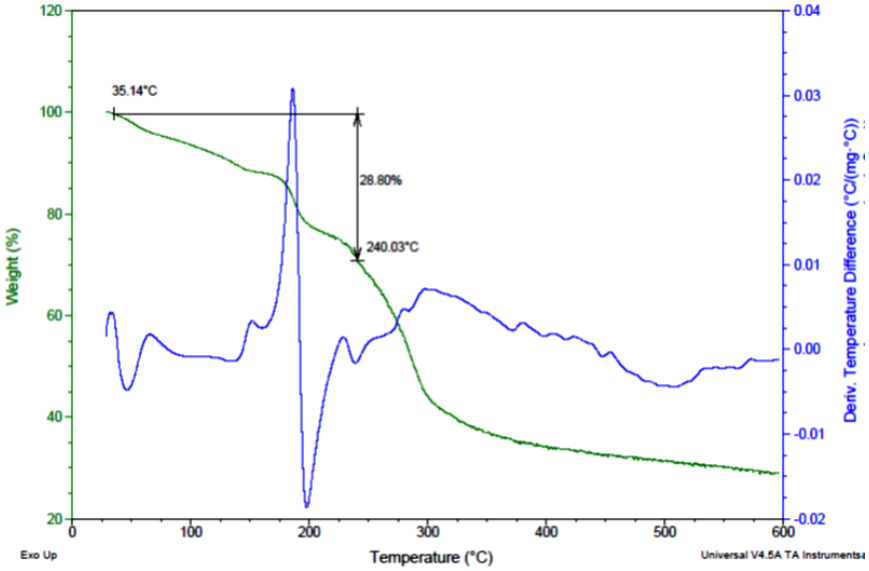


Figure S12: TGA profile of MOP1.

MOP2

Unit cell contents = 32 ligand L2 + 48 anions Br^- + 24 Cu + 5854.6 electrons squeezed from unit cell contributed by the solvent molecules.

Monoclinic *C*2/c space group, Z = 4

Therefore FW = Unitcell contents/Z

= 8 ligand L1 + 12 anion Br^- + 6 Cu + 1396 electrons

(~ 8 DMSO + 90 H_2O molecules)

= 8×564.6 + 12×79.9 + 6×63.546 + 2244.8

= 4516.8+ 958.8+ 381.276 + 2244.8

= 8101.676

Weight loss for 8 DMSO + 90 H_2O molecules

= 2244.8/8101.676 X 100%

= 27.70 % Experimental Value (25.35 %)

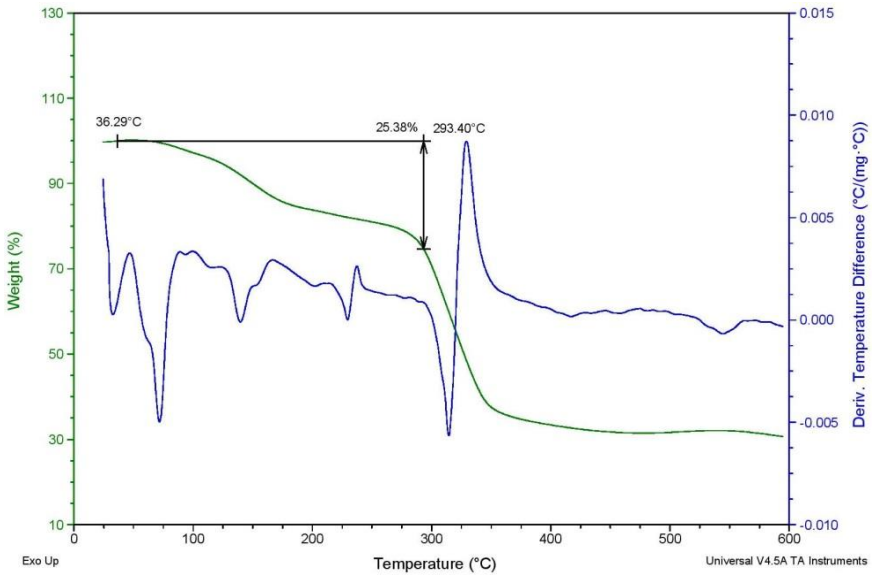


Figure S13: TGA profile of MOP2.

NMR study:

100 mg of the crystals of CPs and MOPs were soaked in 0.5 ml DMSO-d^6 or Methanol-d^4, respectively and then slightly warmed for few minutes.After thet the insoluble CPs and MOPs were filtered off. The filtrates were respectively characterised by NMR spectroscopy.

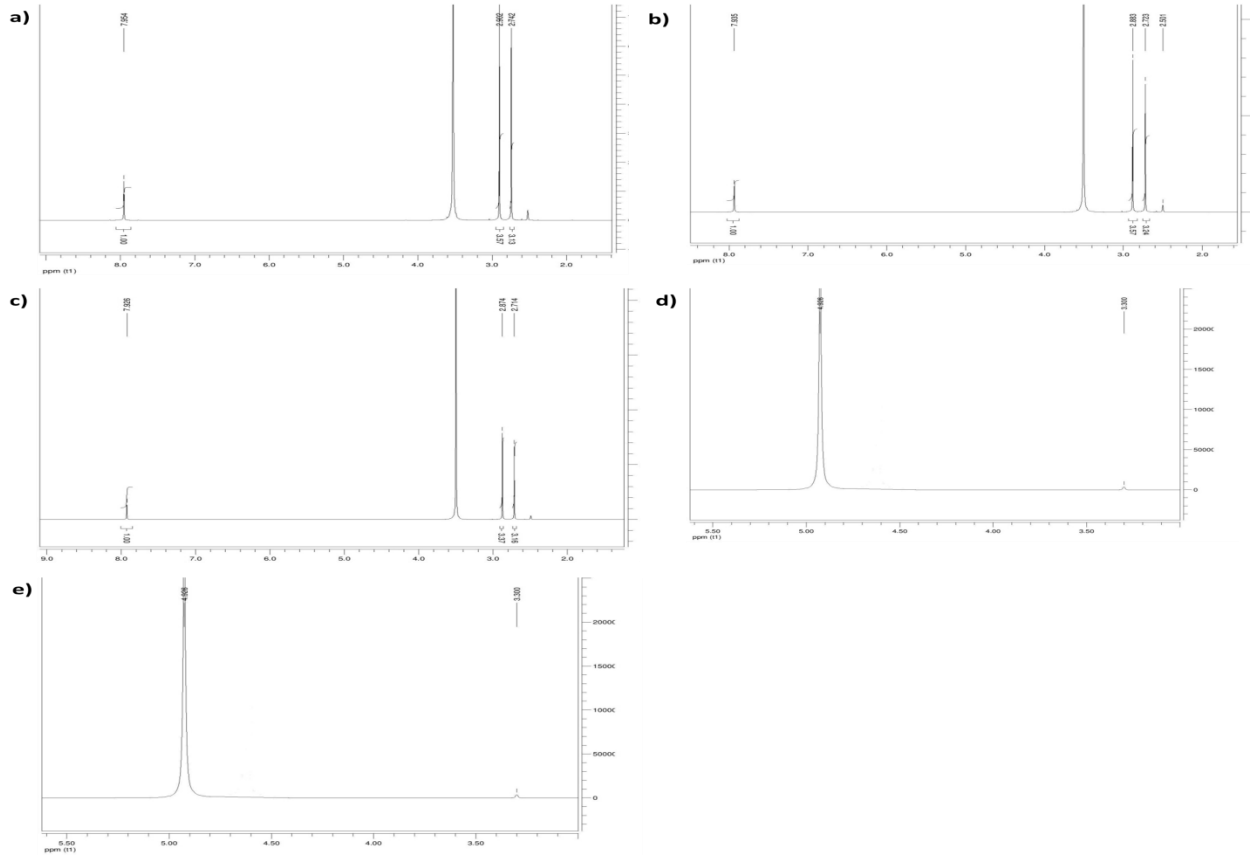


Figure S14: NMR profiles of a) occluded DMF in CP1, b) occluded DMF in CP2, b) occluded DMF in CP3, d) occluded water in MOP1, b) occluded water in MOP2.

Powder X-ray diffraction: PXRD data were collected using Bruker AXS D8 Advance Powder (Cu Kα1 radiation, λ = 1.5406 Å) Diffractometer equipped with super speed LYNXEYE detector. The sample was prepared by making a thin film of finely powdered sample (~30 mg) over a glass slide. The experiment was carried out with a scan speed of 0.3 sec/step (step size = 0.02˚) for the scan range of 5-35˚ 2θ.

PXRD pattern of CP1 - CP3 and MOP1, MOP2.

CP1

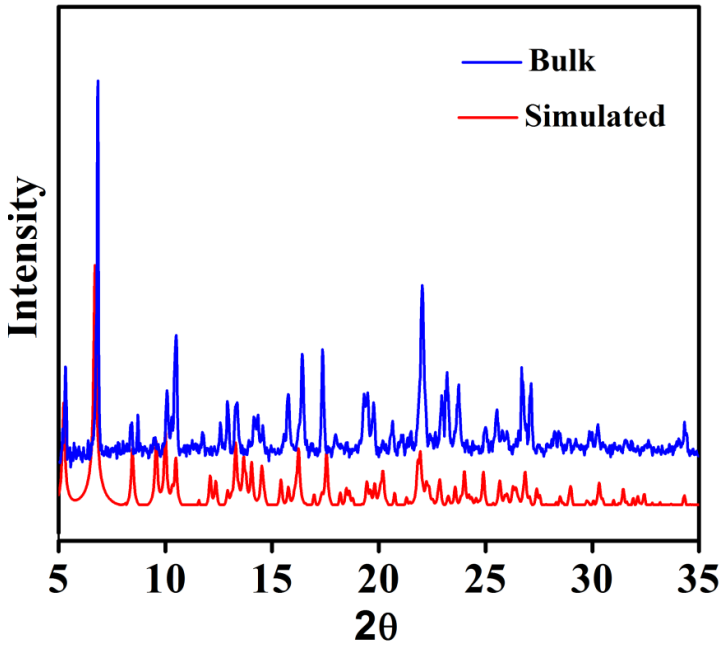


Figure S15: PXRD plot of simulated and bulk for CP1.

CP2

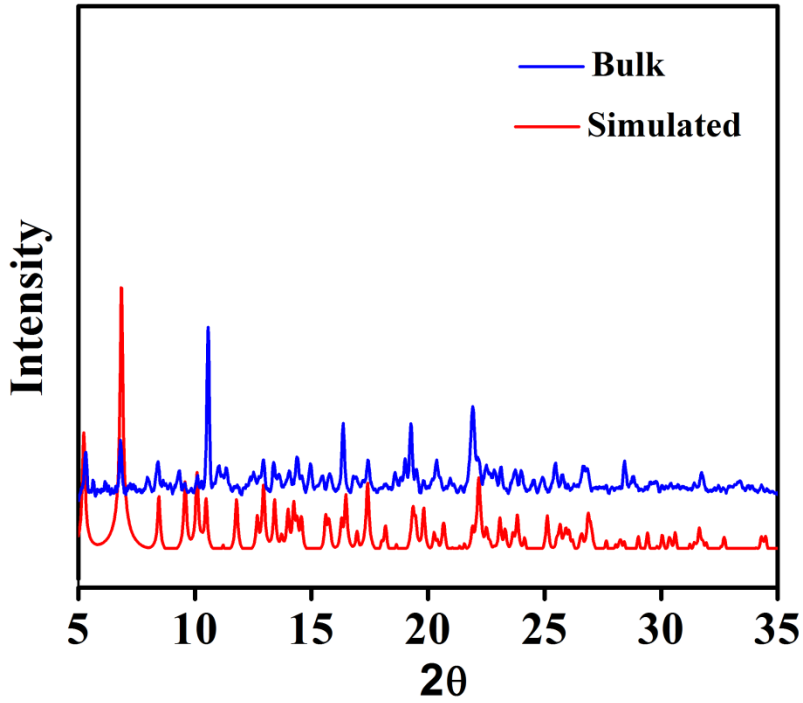


Figure S16: PXRD plot of simulated and bulk for CP2.

CP3

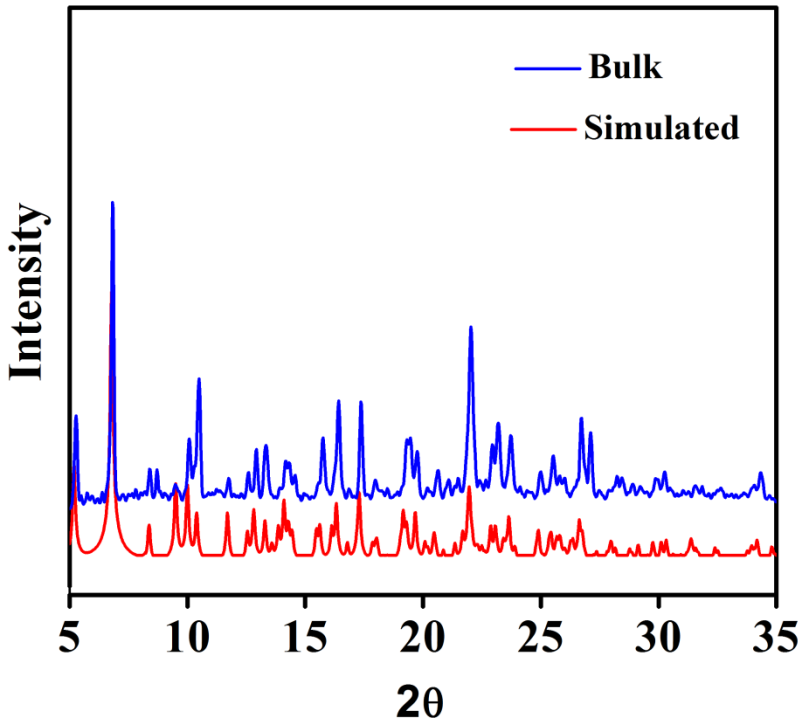


Figure S17: PXRD plot of simulated and bulk for CP3.

MOP1

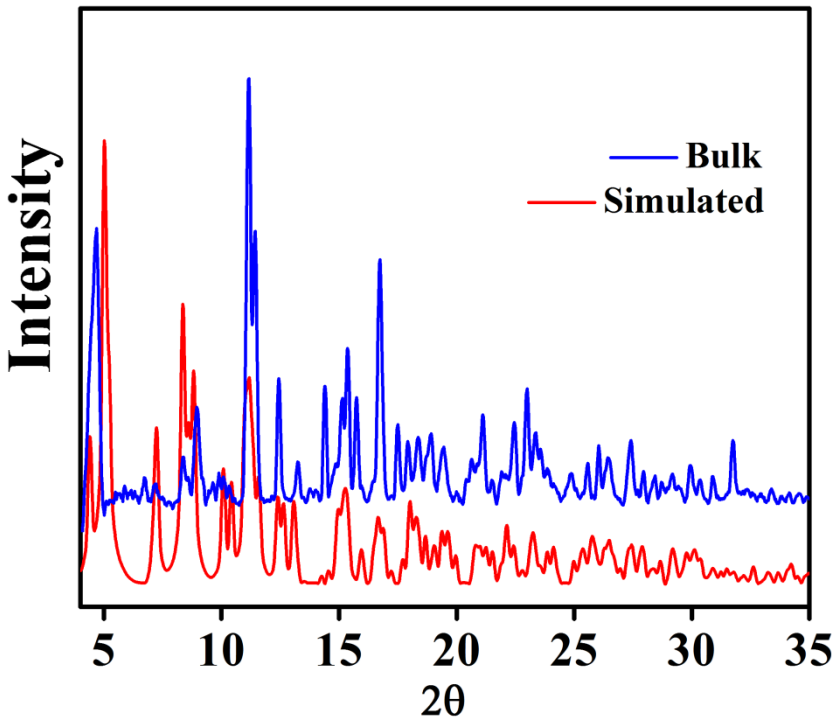


Figure S18: PXRD plot of simulated and bulk for MOP1.

MOP2

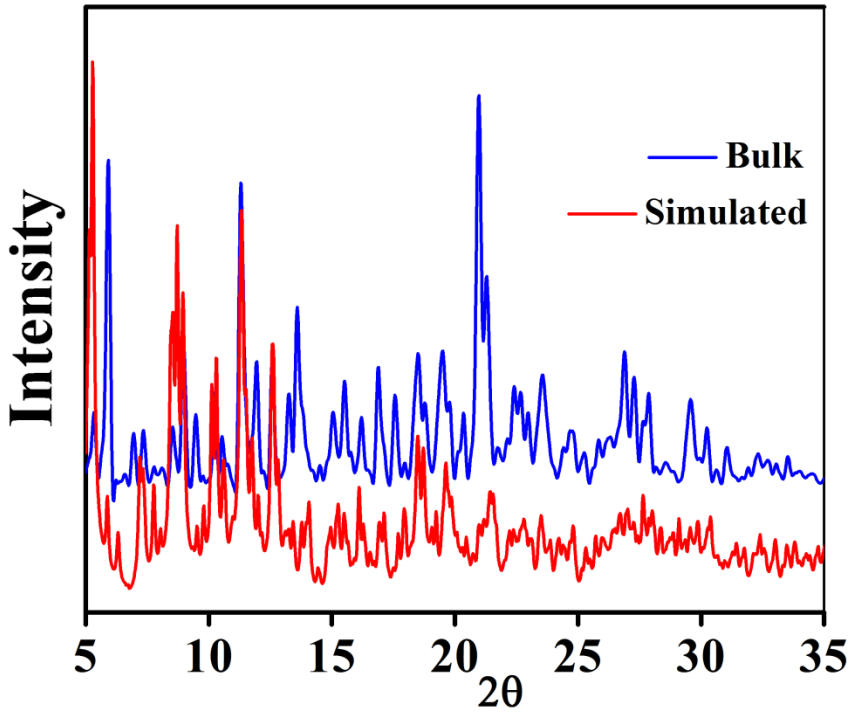


Figure S19: PXRD plot of simulated and bulk for MOP2.

Preparation of vesicles from MOPs:

1 mg of the each MOP was taken in a separate vial and then DMSO was added (Final concentration 180 μM). The resulted solution was then subjected for various analyses like DLS, TEM, and AFM. The stability of the aggregates was studied by DLS measurement. Up to 45 μM concentration, the aggregation was stable and then disintegrated to molecular MOP at 18 μM as evident from DLS and TEM. Vesicle formed from MOP1 and MOP2 hereafter vesicle 1 and vesicle 2, respectively.

TEM sample preparation: The DMSO solution of the corresponding MOPs (concentration = 180 μM) was drop casted on a carbon-coated Cu (300 mesh) TEM grid. The grid was dried under vacuum at room temperature for one day and used for recording TEM images.

Atomic Force Microscopic (AFM) Study: One drop of the DMSO solution of the vesicles was drop-casted on a separate mica and air dried for 24 hours. Then it was subjected for AFM analysis.

TEM images:

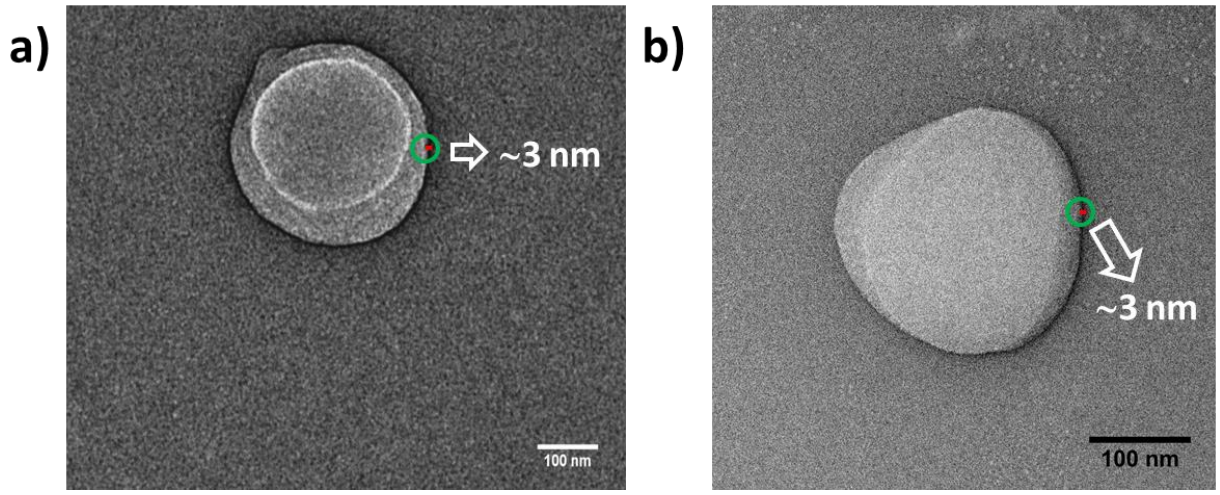
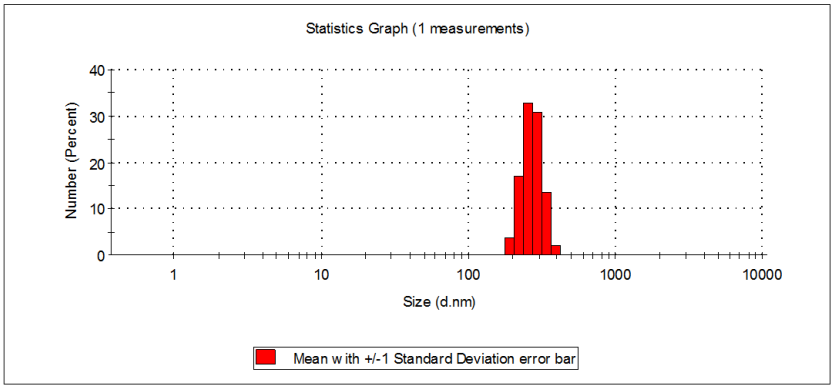


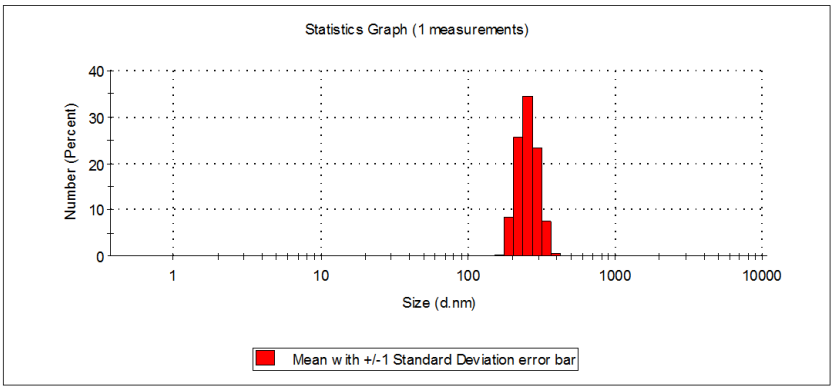
Figure S20: Measurement of wall thickness of a) vesicle 1 and b) vesicle 2.

DLS data:

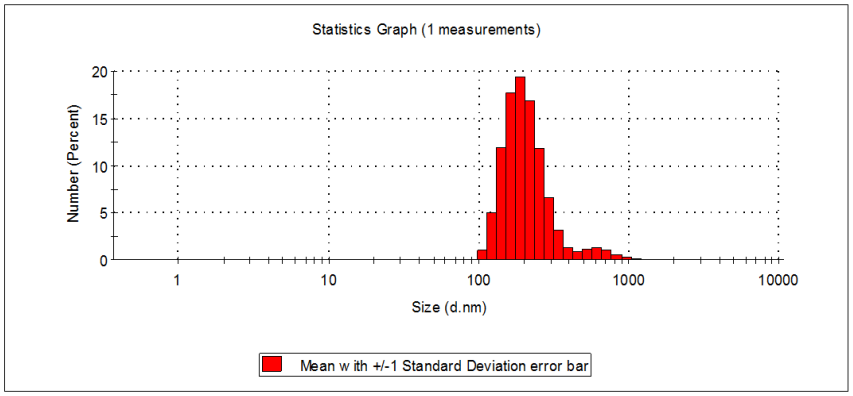
a)



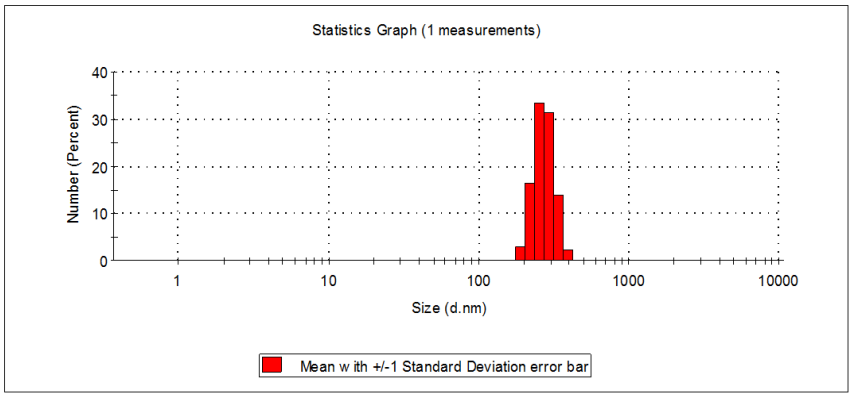
b)



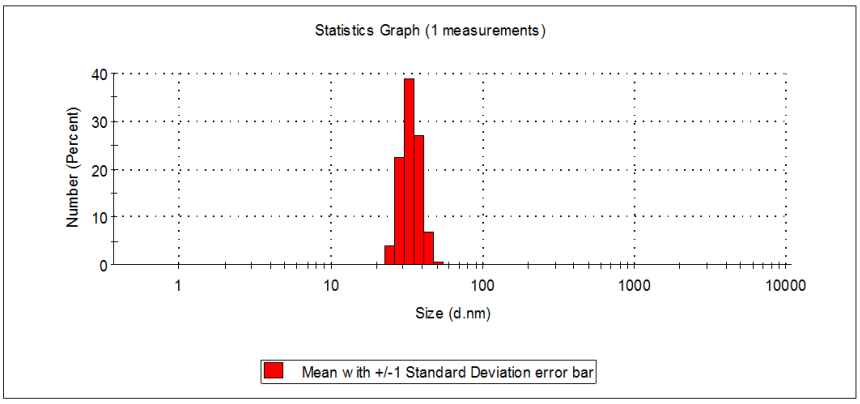
c)



d)



e)



f)

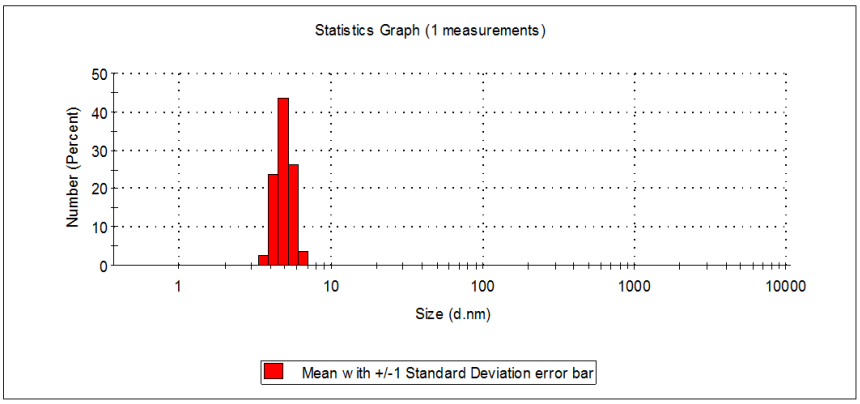
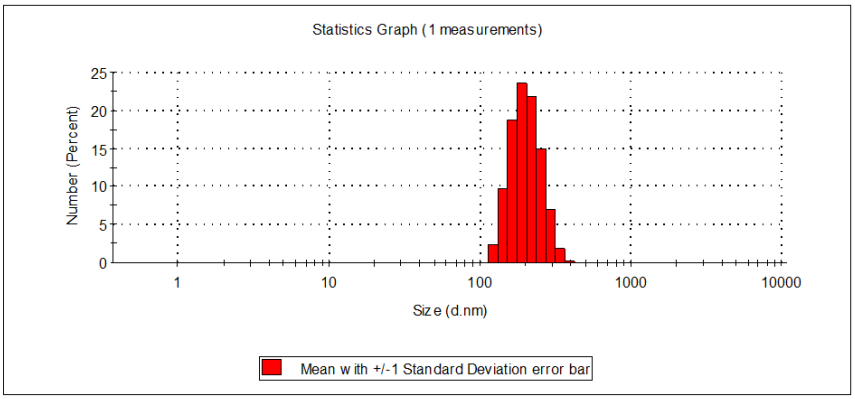
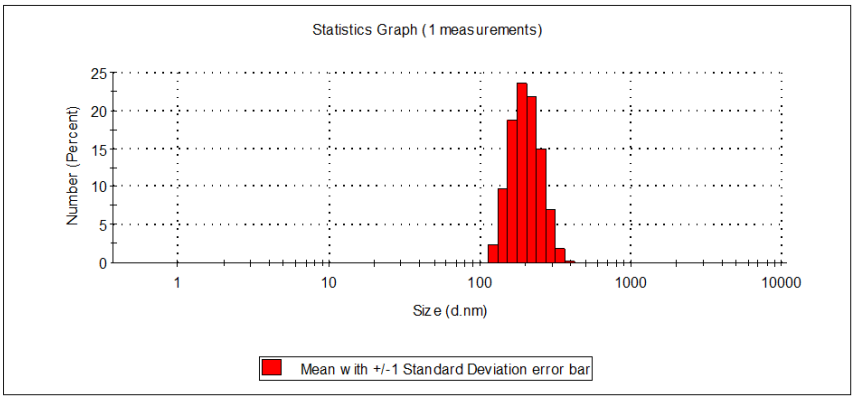


Figure S21: DLS data of a) 180 μM solution, b) 90 μM solution, c) 45 μM solution, d) 50 times dilution of solution (a) (3.6 μM) keeping H_2O: DMSO (98:2), e) 0.45 μM solution, f) 0.18 μM solution of vesicle 1.

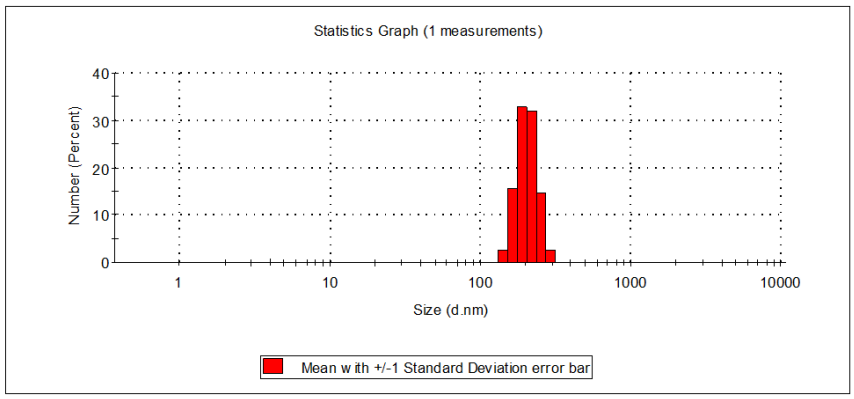
a)


Statistics Graph (1 measurements)
Number (Percent)
25
20
15
10
5
0
1
10
100
1000
10000
Size (d.nm)
Mean with +/-1 Standard Deviation error bar

b)


Statistics Graph (1 measurements)
Number (Percent)
25
20
15
10
5
0
1
10
100
1000
10000
Size (d.nm)
Mean with +/-1 Standard Deviation error bar

c)


Statistics Graph (1 measurements)
Number (Percent)
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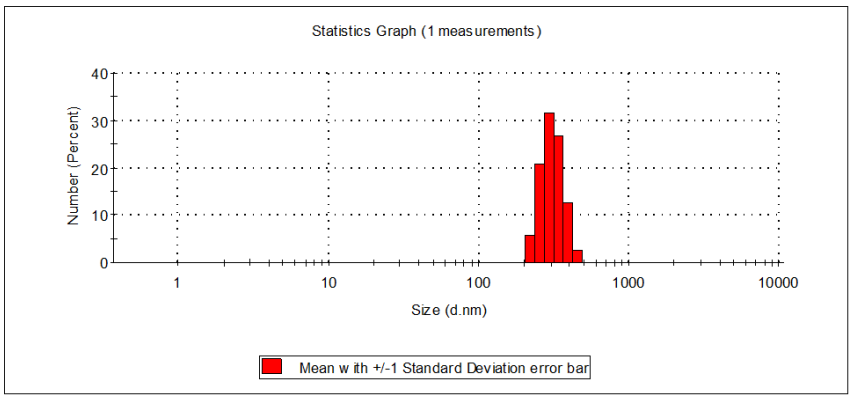
30
20
10
0
1
10
100
1000
10000
Size (d.nm)
Mean with +/-1 Standard Deviation error bar

d)


Statistics Graph (1 measurements)
Number (Percent)
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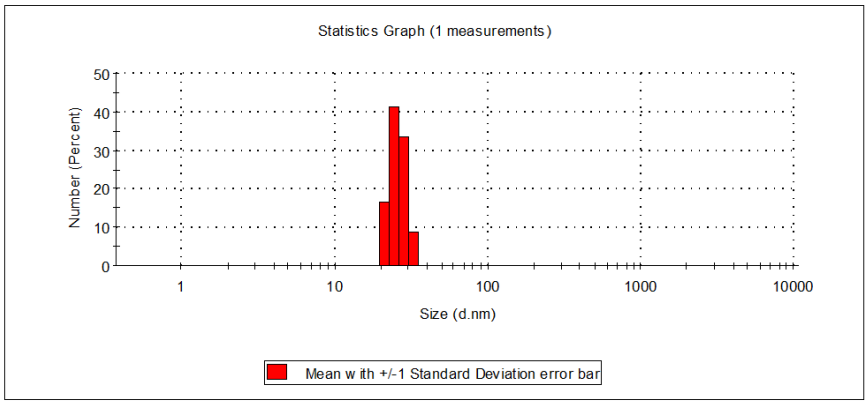
30
20
10
0
1
10
100
1000
10000
Size (d.nm)
Mean with +/-1 Standard Deviation error bar

e)



f)

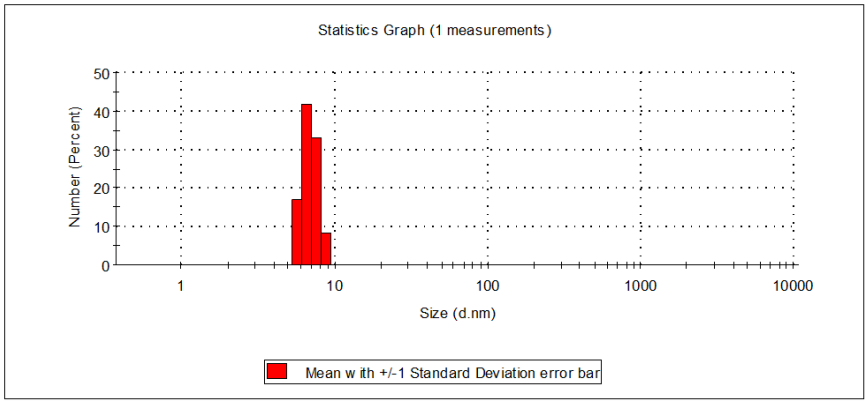
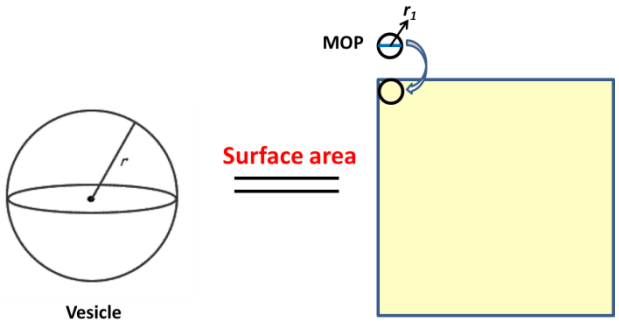


Figure S22: DLS data of a) 180 μM solution, b) 90 μM solution, c) 45 μM solution, d) 50 times dilution of solution (a) (3.6 μM) keeping H_2O: DMSO (98:2), e) 0.45 μM solution, f) 0.18 μM solution of vesicle 2.

Calculation for the number of MOP required for filling the surface of a sphere and a solid sphere:



Surface area of the vesicular architecture may be considered as the surface area of a folded square shaped paper. The surface area of a sphere = $4\pi r^2$ (where r = radius of the sphere).
If MOP is considered as a 2D circle of radius r_1, the surface area of MOP becomes πr_1^2.

So, number of MOP required to fill the square paper = $4\pi r^2/\pi r_1^2$. (Considering closed packed model)

According to DLS study the radius of the vesicular architecture (r) = ~ 150 nm and the radius of the MOP = ~ 2 nm.

So, number of MOP required = 22,640.

Volume of the vesicular architecture = $\frac{4}{3}\pi r^3$.

Volume of one MOP = $\frac{4}{3}\pi r_1^3$.

So, the number of MOP required to fill a solid sphere = 4,20,895. (Considering closed packed model)

TEM images of single nanocages:

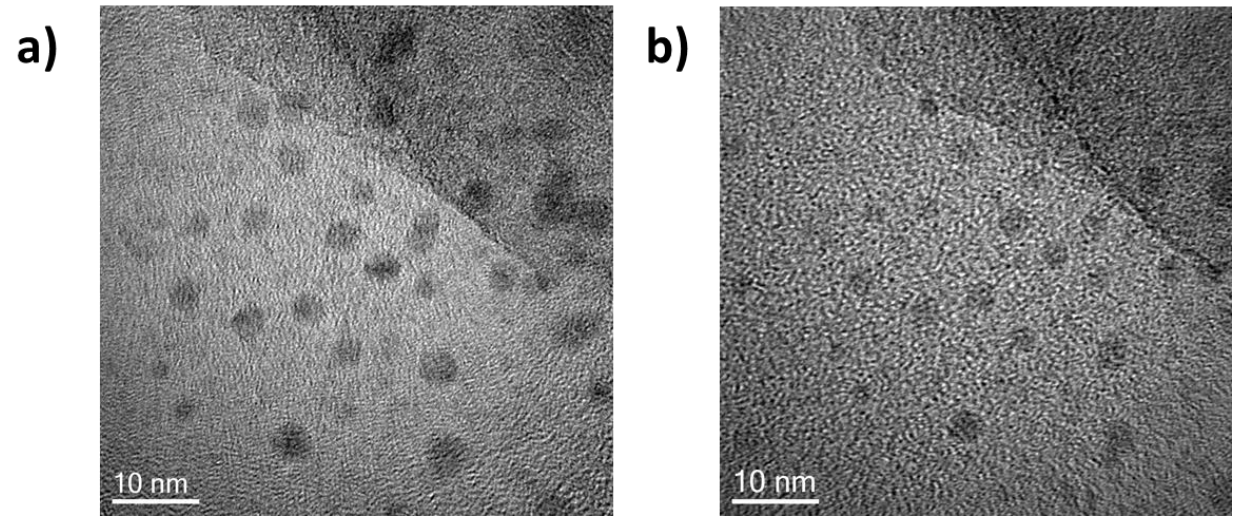


Figure S23: TEM images of the single nanocages of a) Vesicle 1 and b) vesicle 2 obtained from the solution of each vesicle at 0.18 μM concentration.

Calcein encapsulation within the vesicles: 1 mg of the MOP1/MOP2 and 1.3 mg of calcein were taken in a vial and 100 μL DMSO was added. This mixture was further diluted with 1900 μL of water and then subjected to dialysis using SnakeSkin® dialysis tubing with molecular weight cut off 3500 for 72 hours following standard technique. Concentration of Calcein inside the vesicle was estimated from UV-Vis spectra.

<u>Calculation of calcein encapsulation within vesicle 1</u>

From UV-VIS spectroscopy, absorbance of the same concentrated free calcein is (A) 0.01373.

Extinction coefficient (ε) is 77,000 for calcein.

Path length (l) is 1 cm.

From Lambert-beer's law, A = ε.c.l

So, c = A/ε.l

= 0.01373/77000×1

= 1.783X10^{-7} (M).

Encapsulation efficiency = 1.783×10^{-7} (M)/ 2.5X10^{-6} (M)×100%

= 7.13 %

Calculation of calcein encapsulation within vesicle 2

From UV-VIS spectroscopy, absorbance of the same concentrated free calcein is (A) 0.01335.
Extinction coefficient (ε) is 77,000 for calcein.
Path length (l) is 1 cm.
From Lambert-beer's law, A = ε.c.l

So, c = A/ε.l

= 0.01335/77000×1

= 1.73X10^{-7} (M).

Encapsulation efficiency= 1.73×10^{-7}(M)/2.5X10^{-6} (M)×100%

= 6.92 %

Sample preparation for fluorescence microscopy: The DMSO solution of the dye/drug encapsulated vesicles was drop casted on a glass slide. The slide was then dried under vacuum at room temperature for one day and used for recording fluorescence images.

Calcein encapsulation by vesicle 1:

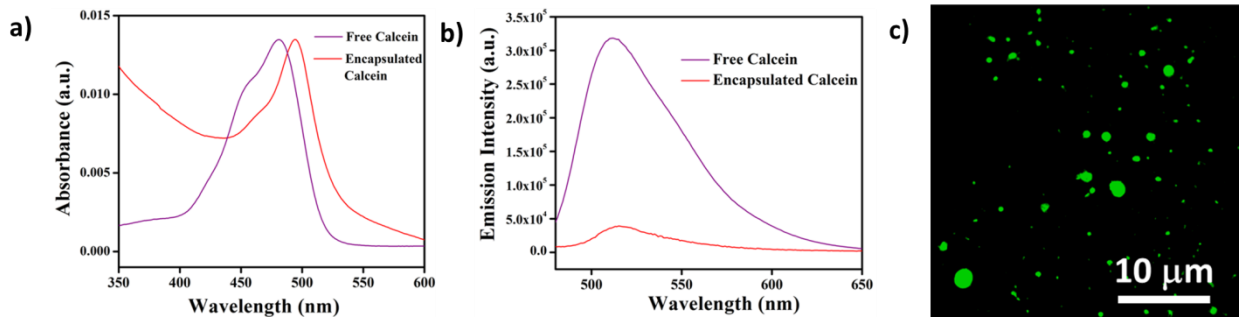


Figure S24: a) UV-Vis and b) Photoluminiscence plot of encapsulated and free calcein in vesicle 2, c) Fluorescence microscopic image after calcein encapsulation within the vesicle 1.

Calcein encapsulation by vesicle 2:

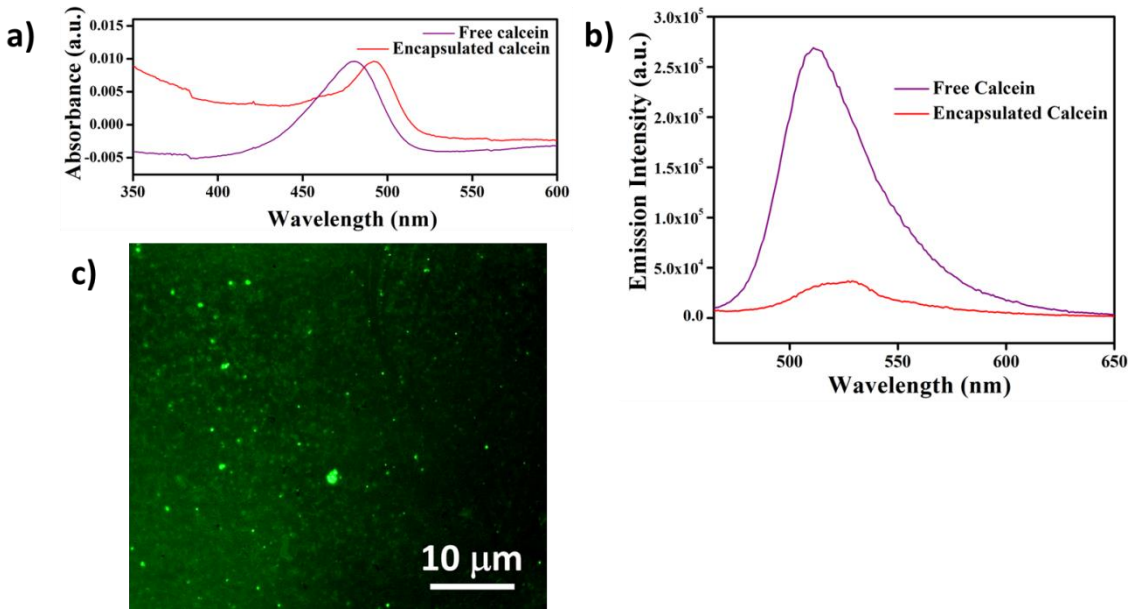
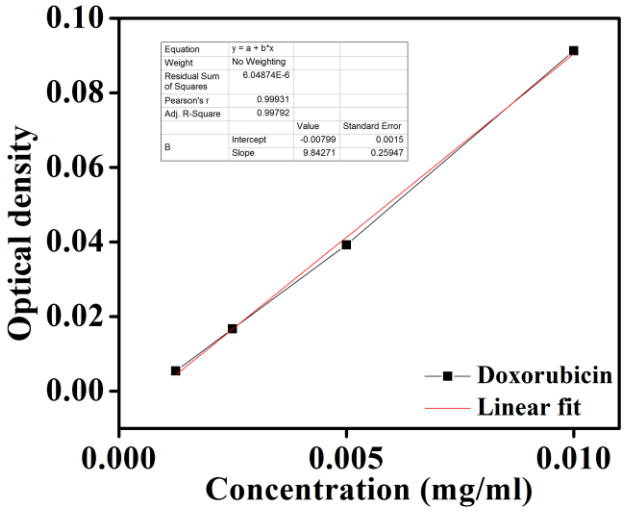


Figure S25: a) UV-Vis and b) Photoluminiscence plot of encapsulated and free calcein in vesicle 2, c) Fluorescence microscopic image after calcein encapsulation within the vesicle 2.

Doxorubicin encapsulation within the vesicle 1:

1 mg of the MOP1/MOP2 and 0.1 mg of doxorubicin.HCl (DOX) were taken in a vial and 100 μL DMSO was added. This mixture was further diluted with 1900 μL of water and then subjected to dialysis using SnakeSkin® dialysis tubing with molecular weight cut off 3500 for 72 hours following standard technique. Concentration of DOX inside the vesicle was estimated from UV-Vis spectra.

<u>Calculation of DOX encapsulation within vesicle 1</u>



From the calibration curve, molar extinction coefficient = 9.84271
Initial concentration of doxorubicin used = 0.05 mg/ml
Final concentration of doxorubicin in vesicle 1 = 9.9769×10^{-4} mg/ml
So, loading efficiency = 1.99%.

Biological studies.

Physiological stability and MTT assay: RAW 264.7 macrophage cells were purchased from American Type Culture Collection (ATCC) and maintained following their guidelines. The cells were cultured in Dulbecco's modified eagle's medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin–streptomycin and kept in a humidified incubator at 37° C and 5% CO_2.

The cytotoxicity of the vesicle 1 and DOX encapsulated vesicle 1 were evaluated in RAW 264.7 cells by using a standard MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. In a 96-well plates, the cells were seeded keeping density approximately 1×10^4 cells per well. After 24 h of seeding, the cells were treated with various concentrations (0.50, 0.60, 0.70 and 1.0 μM) of the vesicle 1/DOX@vesicle 1 or DMEM alone for 72 h in a humidified incubator at 37° C and 5% CO_2. The culture medium was then replaced with 100 mg of MTT per well and kept at 37° C and 5% CO_2 for 4 h. The formazan produced by mitochondrial reductase from live cells was dissolved by adding DMSO (100 mL per well) and incubated for 30 min at 37° C. The absorbance of formazan was recorded at 570 nm by using a multiplate ELISA reader (Varioskan Flash Elisa Reader, Thermo Fisher). The percentages of survival of cells in vesicle 1/DOX@vesicle 1 treated samples were calculated by considering the DMEM-treated sample to be 100%.

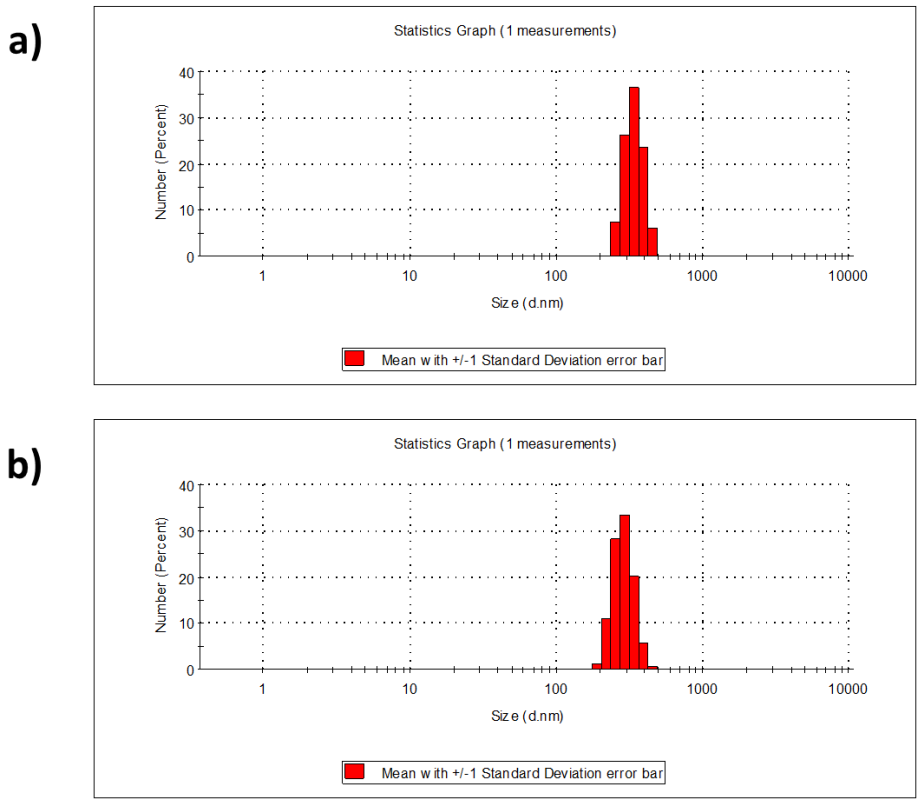


Figure S26: DLS data of a) 180 μM solution of vesicle 1 in PBS buffer (DMSO:PBS = 2:98), b) 180 μM solution of vesicle 2 in PBS buffer (DMSO:PBS = 2:98).

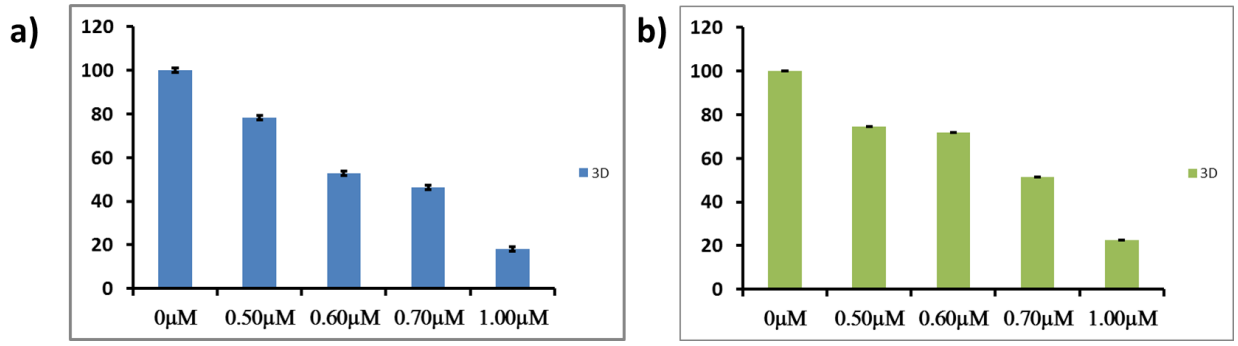


Figure S27: MTT assay a) Vesicle 1, b) DOX encapsulated vesicle 1.

Cell imaging: For cell imaging, RAW 264.7 cells were cultured by using DMEM supplemented with 10% FBS and 1% penicillin–streptomycin on ethanol etched cover slips kept in a 35 mm tissue culture dishes. The dishes were then kept in a humidified incubator at 37° C overnight. Then the cells were washed with PBS and incubated in serum-free media (SFM) for half an hour. DMSO solution of DOX encapsulated vesicle 1 at IC_{50} concentration was made by mixing it in serum-containing medium keeping Serum-containing medium: DMSO = 98:2 (v/v). These

solutions were incubated for 30 min. After incubation, SFM was discarded followed by addition of the media containing the DOX@vesicle 1. The cells were fixed by using 4% paraformaldehyde for 10 min at room temperature. Then the cells were washed with PBS and mounted on glass slides for microscopy.

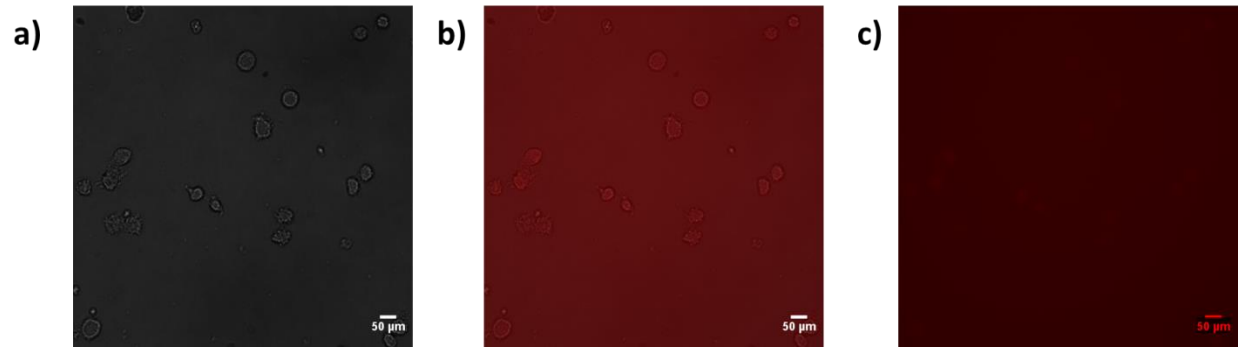


Figure S28: Fluorescent microscopic images of the RAW 264.7 cells displaying a) bright field, b) overlay and c) fluorescence of the images when incubated with the DOX encapsulated vesicle 1 for 4 hours.

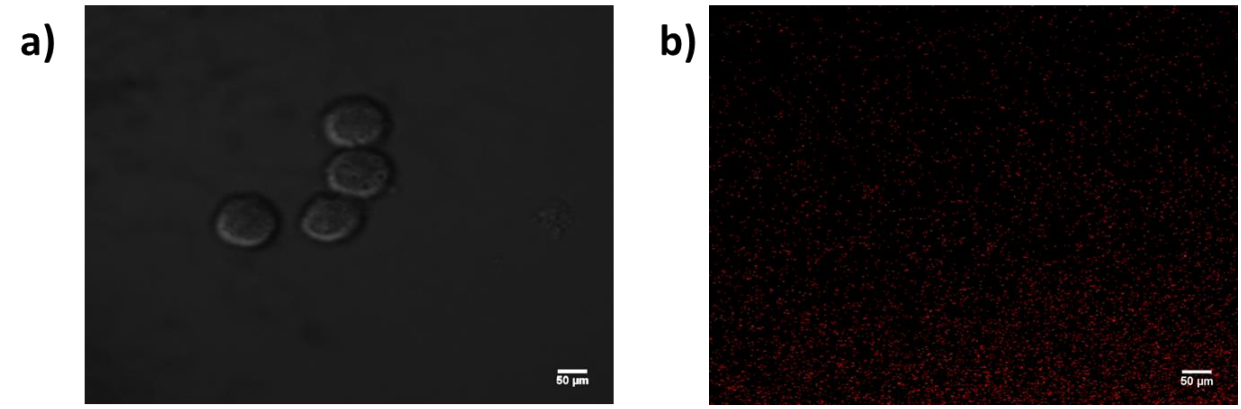


Figure S29: RAW 264.7 cells incubated without DOX displaying no auto-fluorescence. Fluorescence microscopic images of a) bright field, b) fluorescence.

DOX release study:

DMSO stock solution of vesicle 1 was taken in three different vials. 1(N) HCl was then added to convert the pH of the solution to 6, 5 and 4, respectively. The final pH of the solution was checked by litmus paper. These solutions were kept for 30 minutes and then subjected to DLS measurements.

In a separate experiment, five sets of DOX loaded vesicle solution with pH 7, 6, 5, 4, 1 were prepared by following similar procedure as stated above. These solutions were kept for 30 minutes and then subjected to photoluminescence analysis.

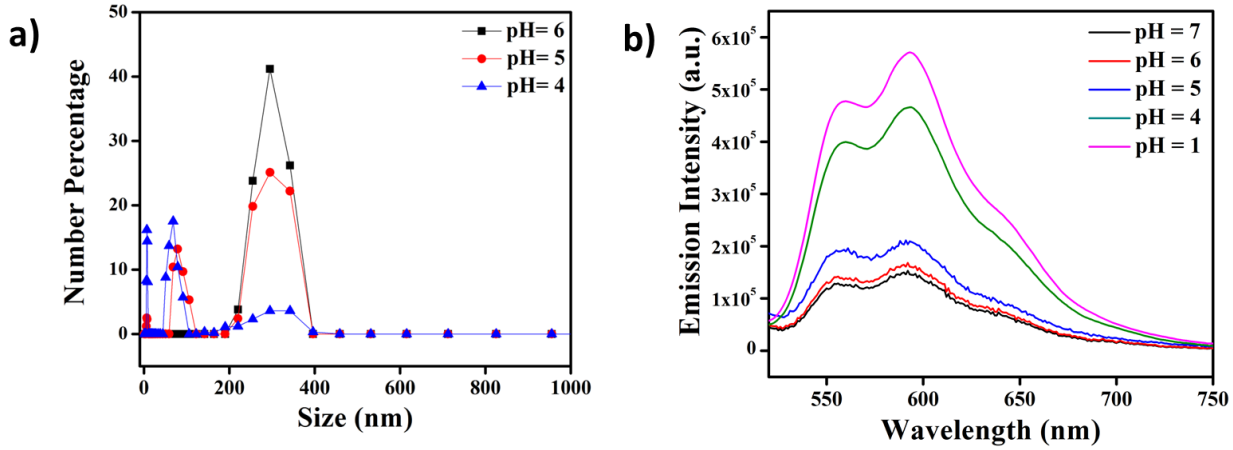


Figure S30: a) DLS data of vesicle 1 at different pH, b) Emission spectra of DOX encapsulated vesicle 1 at different pH.

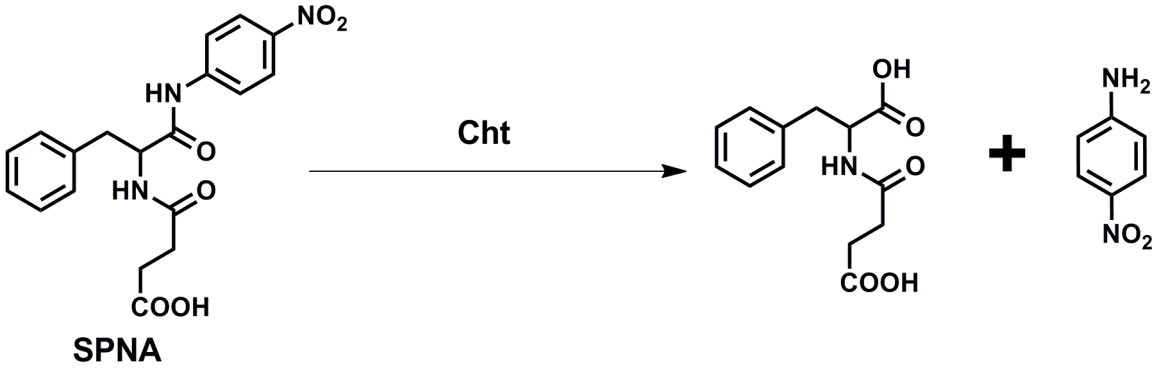
Chymotrypsin inhibition study:

Solution 1 (S1). $1.0x10^{-6}$M solution of Bovine pancreatic α-chymotrypsin (Cht).

Solution 2 (S2). $1.0x10^{-6}$M solution of all vesicles keeping H_2O: DMSO = 98: 2.

Solution 3 (S3). $4.0x10^{-3}$M solution of N-succinyl-l-phenylalanine-para-nitroanilide (SPNA) keeping H_2O: DMSO = 98: 2.

Solution 4 (S4). $2.0x10^{-6}$M solution of NaBr keeping H_2O: DMSO = 98: 2 (Amount of NaBr was taken keeping the no. of moles of Br^- same as that of the vesicle of MOP 2).



10 ml of the α-chymotrypsin solution (S1) was added to 10 ml of each vesicle solutions (S2) and NaBr solution (S4). For the reaction an aliquot (2.00 ml) of these solutions was added to a UV cell. 50µl of S3 was then added (final concentrations were $1.0x10^{-4}$M in SPNA, $5x10^{-7}$M in vesicles and $5x10^{-7}$M in α-chymotrypsin). Also for control reaction 10 ml of S1 was mixed with 10 ml of water and 50µl of the S3 was added. After thorough mixing, solutions were kept undisturbed for 10 minutes. Hydrolysis was followed by monitoring product formation at 410 nm

every 20 seconds (for a total of 1.5 hours) using UV/Vis spectrometry. Form the absorbance value, the concentration of 4-nitro aniline was estimated considering its extinction coefficient 8800 $M^{-1}cm^{-1}$ and plotted against time. The rate of formation of 4-nitro aniline was calculated by calculating the slope of each straight line. The activity of the enzyme was calculated from the ratio of the slope obtained from each experiment with control experiment and multiplying by 100 % (assuming the activity of cht was 100 % in absence of vesicles or NaBr). Inhibition was calculated by subtracting the activity from 100 %. To probe the fact that the enzyme was not denatured during the experiment emission (λ_{ex}= 295 nm) and CD spectra were recorded for a freshly prepared solutions after a mere incubation of 24 h. For thermal denaturation the Cht solution was heated at 90 ° C for 0.5 h and the spectra were recorded. No change in spectral features and spectral features were different from that of the denatured one, indicated the lack of denaturation during the experiment.

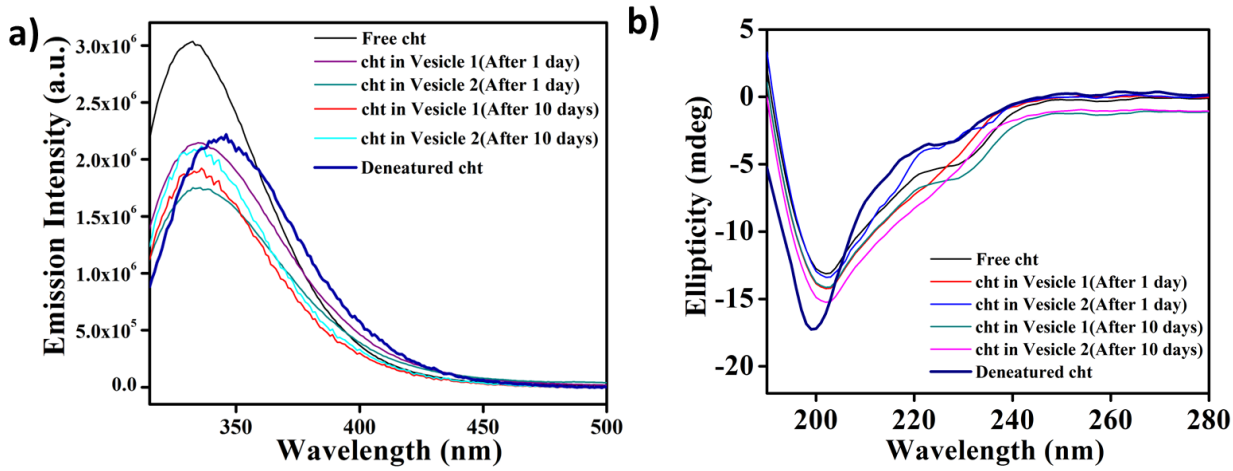


Figure S31: a) Fluorescence spectra (λ_{ex} = 295 nm) and b) CD spectra of Cht in various experimental conditions and that of thermally denatured Cht showing that no denaturation occurred in the experimental conditions.

Calculation for chymotrypsin inhibition study:

Slope determined for control experiment (K_0) = 0.10783
Slope determined for inhibition experiment with NaBr (K_1) = 0.09134
Slope determined for inhibition experiment with vesicle 1 (K_2) = 0.07653
Slope determined for inhibition experiment with vesicle 2 (K_3) = 0.05194

Activity of Cht for control experiment = 100 %
Activity of Cht for inhibition experiment with NaBr = K_1/ K_0 X 100 % = 84.7 %
Activity of Cht for inhibition experiment with vesicle 1 = 0.07653 = K_2/ K_0 X 100 % = 70.9 %
Activity of Cht for inhibition experiment with vesicle 2 = 0.07653 = K_3/ K_0 X 100 % = 53.6 %
Therefore, inhibition of activity caused by NaBr = (100- 84.7) % = 15.3 %
Inhibition of activity caused by vesicle 1 = (100- 70.9) % = 29.1 %
Inhibition of activity caused by vesicle 1 = (100- 53.6) % = 46.4 %

Checkcif reports:
CP1

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: CP-1

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Bond precision:  C-C = 0.0056 A          Wavelength=0.71073

Cell:            a=36.068(8)     b=14.096(3)          c=16.023(4)
                 alpha=90        beta=109.397(7)      gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	7684(3)	7684(3)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C60 H60 Cl2 Cu N12 O14	0.5(C120 H120 Cu2 N24 O12), 2(Cl O4)
Sum formula	C60 H60 Cl2 Cu N12 O14	C60 H60 Cl2 Cu N12 O14
Mr	1307.65	1307.64
Dx,g cm-3	1.130	1.130
Z	4	4
Mu (mm-1)	0.414	0.414
F000	2716.0	2716.0
F000'	2719.61	
h,k,lmax	48,18,21	47,18,21
Nref	9539	9360
Tmin,Tmax	0.862,0.921	0.548,0.746
Tmin'	0.862	

```
Correction method= # Reported T Limits: Tmin=0.548 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.981          Theta(max)= 28.274

R(reflections)= 0.0873( 5067)     wR2(reflections)= 0.2843( 9360)

S = 1.018                 Npar= 487
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) .... 3 Report

Author Response: Some atom couldn't be refined anisotropically as anisotropic \ refinement doesnot improve the model statistics.

Alert level C

RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25
Weighted R factor given 0.284

Author Response: This is due to poor data quality. Multiple collection of the data \ couldn't improve the data quality.

PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.28 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range 4.1 Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C16 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of O4 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N5 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C20 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C26 Check
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H9C .. H23B .. 2.13 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor N2 -- H2 ... Please Check

---

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 3 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.18 Report
PLAT230_ALERT_2_G Hirshfeld Test Diff for Cl1A -- O4 .. 15.2 s.u.
PLAT230_ALERT_2_G Hirshfeld Test Diff for Cl1B -- O4 .. 8.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Cu1 -- O4 .. 7.7 s.u.
PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 27 Note
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
10 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
11 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
13 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

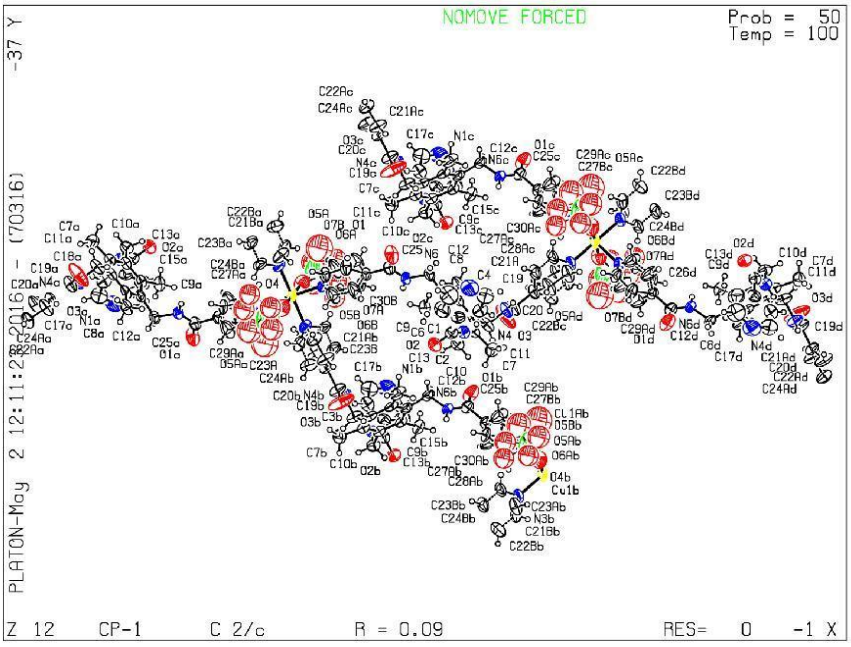
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock CP-1 - ellipsoid plot



CP2

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: CP-2

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Temperature:    100 K

                Calculated                 Reported
Volume          7479.8(11)                 7479.9(11)
Space group     C 2/c                      C 2/c
Hall group      -C 2yc                     -C 2yc
Moiety formula  C60 H60 B2 Cu F8 N12 O6    0.5(C120 H120 Cu2 N24
                                           O12), 2(B F4)
Sum formula     C60 H60 B2 Cu F8 N12 O6    C60 H60 B2 Cu F8 N12 O6
Mr              1282.37                    1282.36
Dx,g cm-3       1.139                      1.139
Z               4                          4
Mu (mm-1)       0.362                      0.362
F000            2652.0                     2652.0
F000'           2654.62
h,k,lmax        37,14,16                   37,14,16
Nref            4429                       4430
Tmin,Tmax       0.891,0.937                0.668,0.745
Tmin'           0.891

Correction method= # Reported T Limits: Tmin=0.668 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 21.726

R(reflections)= 0.0819( 2714)     wR2(reflections)= 0.2587( 4430)

S = 1.041                 Npar= 468
```

```
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level A

```
THETM01_ALERT_3_A  The value of sine(theta_max)/wavelength is less than 0.550
           Calculated sin(theta_max)/wavelength =    0.5208
```

Author Response: The crystal is poorly diffracting. Multiple collection of data with \ more X-ray exposure doesn't improve data quality.

Alert level B

```
PLAT213_ALERT_2_B Atom C4             has ADP max/min Ratio .....       4.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ data quality.

Alert level C

```
REFNR01_ALERT_3_C  Ratio of reflections to parameters is < 10 for a
           centrosymmetric structure
           sine(theta)/lambda              0.5208
           Proportion of unique data used  1.0000
           Ratio reflections to parameters 9.4658
RFACR01_ALERT_3_C  The value of the weighted R factor is > 0.25
           Weighted R factor given   0.259
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full          ! Check
PLAT031_ALERT_4_C Refined Extinction Parameter within Range ......     3.250 Sigma
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................      0.26 Report
PLAT088_ALERT_3_C Poor Data / Parameter Ratio ....................      9.46 Note
PLAT213_ALERT_2_C Atom F3             has ADP max/min Ratio .....       3.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ data quality.

```
PLAT213_ALERT_2_C Atom C3             has ADP max/min Ratio .....       3.2 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ data quality.

```
PLAT213_ALERT_2_C Atom C15B           has ADP max/min Ratio .....       3.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ data quality.

```
PLAT213_ALERT_2_C Atom C18B           has ADP max/min Ratio .....       3.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ data quality.

```
PLAT220_ALERT_2_C Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        3.6 Ratio
PLAT220_ALERT_2_C Non-Solvent Resd 1   F   Ueq(max)/Ueq(min) Range        3.4 Ratio
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         F1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N3 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00779 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N6     --  H6     ...     Please Check
```

Alert level G

```
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          3 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.17 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group     C2/c       I2/a Note
PLAT242_ALERT_2_G Low    'MainMol' Ueq as Compared to Neighbors of         B5 Check
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =              18 Note
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3     ..  C16B    ..       2.68 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3     ..  C15B    ..       2.91 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact  F3     ..  C23A    ..       2.95 Ang.
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
```

```
  1 ALERT level A = Most likely a serious problem - resolve or explain
  1 ALERT level B = A potentially serious problem, consider carefully
 17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 12 ALERT level G = General information/check it is not something unexpected

  2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 16 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
  4 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

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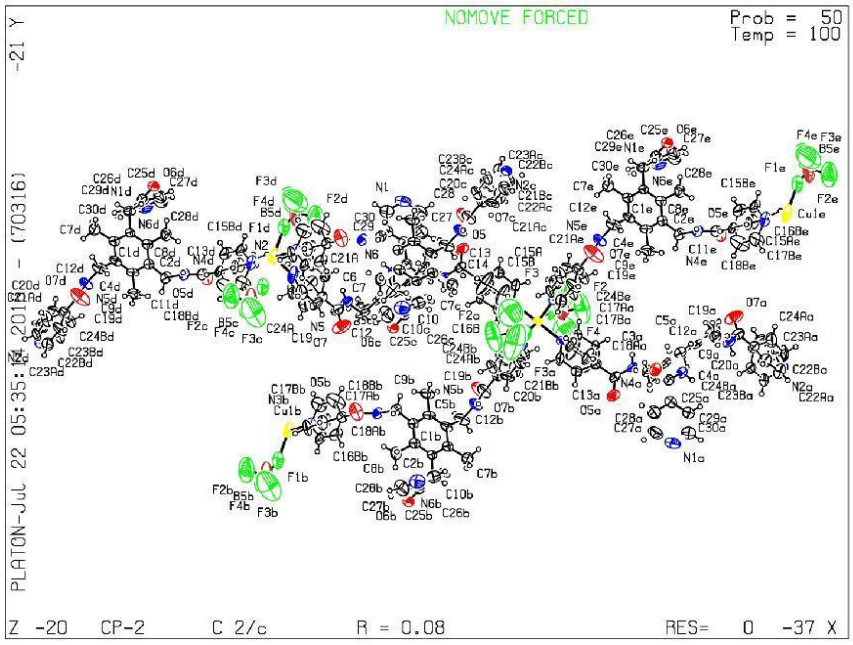
PLATON version of 08/07/2016; check.def file version of 05/07/2016

Datablock CP-2 - ellipsoid plot



CP3

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: CP-3

```
Bond precision:  C-C = 0.0118 A          Wavelength=0.71073

Cell:           a=35.509(10)     b=14.304(4)          c=15.395(4)
                alpha=90         beta=108.369(19)     gamma=90
Temperature:    100 K
```

	Calculated	Reported
Volume	7421(4)	7421(4)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C60 H60 Cu N14 O12	0.5(C120 H120 Cu2 N24 O12), 2(N O3)
Sum formula	C60 H60 Cu N14 O12	C60 H60 Cu N14 O12
Mr	1232.77	1232.76
Dx,g cm-3	1.103	1.103
Z	4	4
Mu (mm-1)	0.354	0.354
F000	2572.0	2572.0
F000'	2574.34	
h,k,lmax	38,15,16	38,15,16
Nref	5064	4893
Tmin,Tmax	0.880,0.932	0.450,0.745
Tmin'	0.880	

```
Correction method= # Reported T Limits: Tmin=0.450 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.966          Theta(max)= 22.835

R(reflections)= 0.0844( 2306)     wR2(reflections)= 0.2962( 4893)

S = 0.985                Npar= 469
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.5460

Author Response: The crystal is poorly diffracting. Multiple collection of data with \ more X-ray exposure doesn't improve data quality.

Alert level B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) ..... 2 Report

Author Response: Some atom couldn't be refined anisotropically as anisotropic \ refinement doesnot improve the model statistics.

Alert level C

RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25
Weighted R factor given 0.296

Author Response: This is due to poor data quality. Multiple collection of the data \ couldn't improve the data quality.

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.139
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full ! Check
PLAT020_ALERT_3_C The value of Rint is greater than 0.12 ..... 0.139 Report
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low .. 47 %
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.30 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range 3.2 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for O4 -- N7 .. 6.5 s.u.
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cu1 -- O4 .. 7.7 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference N3 -- C22B .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N5 -- C27B .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C1 -- C11 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C15 -- C16 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C26 -- C28B .. 0.22 Ang.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of O4 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N3 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N7 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C14 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C20 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C26 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.01184 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C19 - C20 .. 1.53 Ang.
PLAT411_ALERT_2_C Short Inter H...H Contact H16 .. H16 .. 2.13 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor N2 -- H2 ... Please Check

---

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          3 Report
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          2 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          3 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.17 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group     C2/c       I2/a Note
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          2 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..... Percentage =         23 Note
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
```

```
  1 ALERT level A = Most likely a serious problem - resolve or explain
  1 ALERT level B = A potentially serious problem, consider carefully
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  2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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  8 ALERT type 3 Indicator that the structure quality may be low
  9 ALERT type 4 Improvement, methodology, query or suggestion
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```

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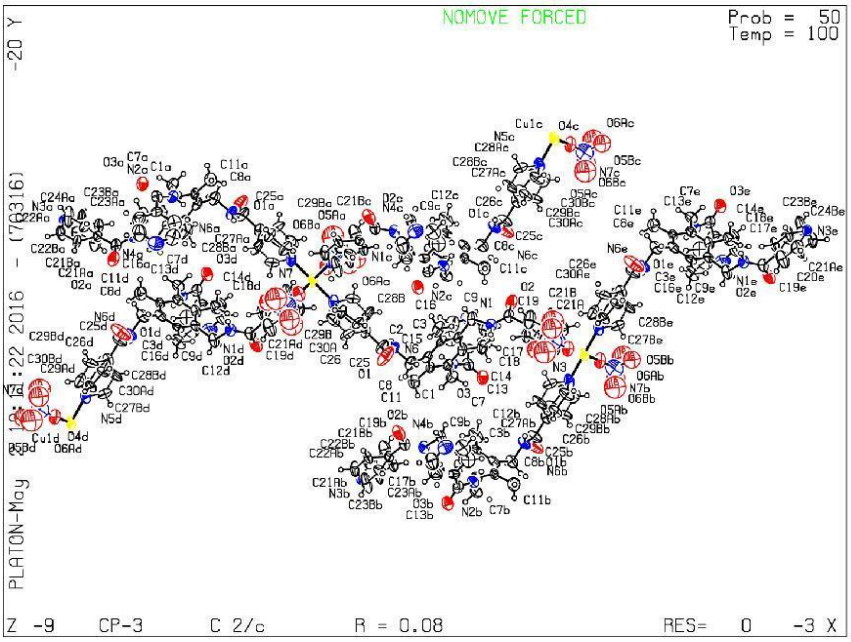
PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock CP-3 - ellipsoid plot



MOP1

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: MOP-TO-1

```
Bond precision:  C-C = 0.0152 A          Wavelength=0.71073

Cell:         a=24.331(3)        b=24.388(3)      c=24.415(3)
              alpha=118.745(2)   beta=91.861(2)   gamma=118.748(2)
Temperature:  120 K

                Calculated                Reported
Volume          10460(2)                  10461(2)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C264 H288 Cl6 Cu6 N48 O30, C264 H288 Cl6 Cu6 N48 O24,
                6(N O3)                   6(N O3), 6(H2O)
Sum formula     C264 H288 Cl6 Cu6 N54 O48 C264 H300 Cl6 Cu6 N54 O48
Mr              5579.50                   5591.59
Dx,g cm-3       0.886                     0.886
Z               1                         1
Mu (mm-1)       0.392                     0.392
F000            2910.0                    2910.0
F000'           2913.91
h,k,lmax        27,27,27                  27,26,27
Nref            31111                     17221
Tmin,Tmax       0.852,0.917               0.478,0.745
Tmin'           0.822

Correction method= # Reported T Limits: Tmin=0.478 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.554          Theta(max)= 23.542

R(reflections)= 0.0823( 9236)     wR2(reflections)= 0.2475( 17221)

S = 0.977                 Npar= 1714
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575
Calculated sin(theta_max)/wavelength = 0.5620

Author Response: The crystal is poorly diffracting. Multiple collection of data with \ more X-ray exposure doesn't improve data quality.

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01522 Ang.

Author Response: This alert is due to poor data quality.

PLAT410_ALERT_2_B Short Intra H...H Contact H8A .. H12Q .. 1.83 Ang.
PLAT410_ALERT_2_B Short Intra H...H Contact H40A .. H45B .. 1.86 Ang.
PLAT410_ALERT_2_B Short Intra H...H Contact H67A .. H74B .. 1.89 Ang.

Alert level C

PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full ! Check
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.9 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 1 H Uiso(max)/Uiso(min) Range 4.4 Ratio
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cu3 -- N21_a .. 5.5 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference O4 -- C76 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O11 -- C16 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N7 -- C26 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N8 -- C22 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N19 -- C80 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C10 -- C11 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C38 -- C39 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C86 -- C87 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C107 -- C108 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C123 -- C124 .. 0.16 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of N8 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C33 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C91 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Cu1 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Cu2 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Cu3 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N25 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N26 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N27 Check
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C123 - C124 .. 1.43 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C28 - C29 .. 1.55 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C88 - C89 .. 1.54 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C109 - C110 .. 1.56 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H7A .. H12P .. 1.96 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H7B .. H14A .. 1.91 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H10A .. H12A .. 1.90 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H10C .. H12D .. 1.95 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H10E .. H12I .. 1.93 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H10F .. H12C .. 1.90 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H42A .. H43B .. 1.98 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H69A .. H72A .. 1.93 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X H23 .. H93 .. 1.99 Ang.

```
PLAT420_ALERT_2_C D-H Without Acceptor       N3     --  H3     ...     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N10    --  H10    ...     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N14    --  H14    ...     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N16    --  H16    ...     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N18    --  H18    ...     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N20    --  H20    ...     Please Check
```

Alert level G

```
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C264 H300 Cl6 Cu6 N54 O48
           Atom count from the _atom_site data:  C264 H288 Cl6 Cu6 N54 O48
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
          From the CIF: _cell_formula_units_Z    1
          From the CIF: _chemical_formula_sum  C264 H300 Cl6 Cu6 N54 O48
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C        264.00    264.00    0.00
          H        300.00    288.00   12.00
          Cl         6.00      6.00    0.00
          Cu         6.00      6.00    0.00
          N         54.00     54.00    0.00
          O         48.00     48.00    0.00
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          2 Note
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............         12 Report
PLAT041_ALERT_1_G Calc. and Reported SumFormula    Strings  Differ     Please Check
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.14 Report
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.002 Degree
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu1    --  C11     ..       12.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu2    --  C12     ..       18.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Cu3    --  C13     ..       22.3 s.u.
PLAT432_ALERT_2_G Short Inter X...Y Contact  O11    ..  C27     ..       3.00 Ang.
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1     (II)    .....       2.51 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu2     (II)    .....       2.25 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu3     (II)    .....       2.24 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          1 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed           ! Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   5 ALERT level B = A potentially serious problem, consider carefully
  42 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  20 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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   4 ALERT type 3 Indicator that the structure quality may be low
  16 ALERT type 4 Improvement, methodology, query or suggestion
   4 ALERT type 5 Informative message, check
```

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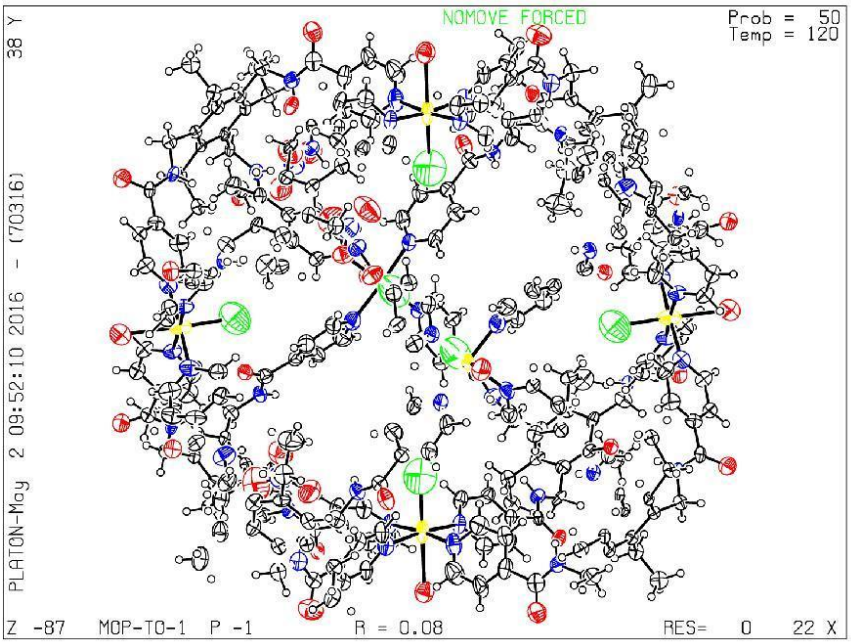
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock MOP-TO-1 - ellipsoid plot



MOP2

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: MOP-TO-2

```
Bond precision:  C-C = 0.0201 A          Wavelength=0.71073

Cell:            a=34.915(3)     b=33.412(3)         c=34.291(3)
                 alpha=90        beta=90.352(4)      gamma=90
Temperature:     120 K

                Calculated                Reported
Volume          40002(6)                  40002(5)
Space group     C 2/c                     C 2/c
Hall group      -C 2yc                    -C 2yc
Moiety formula  C264 H286 Br6 Cu6 N48 O24, C264 H290 Br6 Cu6 N48 O24,
                6(Br)                     6(Br)
Sum formula     C264 H286 Br12 Cu6 N48 O24C264 H290 Br12 Cu6 N48 O24
Mr              5855.53                   5859.58
Dx,g cm-3       0.972                     0.972
Z               4                         4
Mu (mm-1)       1.560                     1.560
F000            11968.0                   11968.0
F000'           11965.73
h,k,lmax        30,29,30                  30,29,30
Nref            14588                     14367
Tmin,Tmax       0.576,0.709               0.575,0.744
Tmin'           0.491

Correction method= # Reported T Limits: Tmin=0.575 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.985          Theta(max)= 18.352

R(reflections)= 0.0842( 12005)    wR2(reflections)= 0.2350( 14367)

S = 1.032                 Npar= 1569
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4430

Author Response: The crystal is poorly diffracting. Multiple collection of data with \ more X-ray exposure doesn't improve data quality.

Alert level B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) ..... 8 Report

Author Response: Some atom couldn't be refined anisotropically as anisotropic \ refinement doesnot improve the model statistics.

PLAT213_ALERT_2_B Atom N17 has ADP max/min Ratio ..... 4.2 prolat

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

PLAT213_ALERT_2_B Atom C1 has ADP max/min Ratio ..... 4.3 prolat

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

PLAT213_ALERT_2_B Atom C5 has ADP max/min Ratio ..... 4.4 prolat

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

PLAT213_ALERT_2_B Atom C48 has ADP max/min Ratio ..... 4.1 prolat

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

PLAT213_ALERT_2_B Atom C57 has ADP max/min Ratio ..... 4.3 prolat

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

PLAT213_ALERT_2_B Atom C72 has ADP max/min Ratio ..... 4.4 oblate

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT220_ALERT_2_B Non-Solvent Resd 1   C   Ueq(max)/Ueq(min) Range        7.4 Ratio
PLAT341_ALERT_3_B Low Bond Precision on  C-C Bonds ..............    0.02011 Ang.
```

Author Response: This alert is due to poor data quality.

```
PLAT410_ALERT_2_B Short Intra H...H Contact  Hj     ..  Hx      ..       1.88 Ang.
PLAT410_ALERT_2_B Short Intra H...H Contact  H0EA   ..  H6EA    ..       1.86 Ang.
```

Alert level C

```
REFNR01_ALERT_3_C  Ratio of reflections to parameters is < 10 for a
           centrosymmetric structure
           sine(theta)/lambda               0.4430
           Proportion of unique data used   1.0000
           Ratio reflections to parameters  9.1568
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full          ! Check
PLAT088_ALERT_3_C Poor Data / Parameter Ratio ....................      9.30 Note
PLAT213_ALERT_2_C Atom Cu3            has ADP max/min Ratio .....       3.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom N13            has ADP max/min Ratio .....       3.6 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom N23            has ADP max/min Ratio .....       3.1 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C3             has ADP max/min Ratio .....       3.7 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C43            has ADP max/min Ratio .....       3.3 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C45            has ADP max/min Ratio .....       3.4 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C74            has ADP max/min Ratio .....       3.7 prolat
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C109           has ADP max/min Ratio .....       3.3 oblate
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT213_ALERT_2_C Atom C132           has ADP max/min Ratio .....       3.3 oblate
```

Author Response: We are chemically sure about the element. This alert is due to poor \ diffraction from the crystal.

```
PLAT220_ALERT_2_C Non-Solvent Resd 1   N   Ueq(max)/Ueq(min) Range        3.2 Ratio
PLAT220_ALERT_2_C Non-Solvent Resd 1   O   Ueq(max)/Ueq(min) Range        3.6 Ratio
PLAT222_ALERT_3_C Non-Solvent Resd 1   H Uiso(max)/Uiso(min) Range        6.0 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C59    --  C63     ..        5.3 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference O1     --  C31     ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O4     --  C42     ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O5     --  C58     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O8     --  C102    ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1     --  C134    ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N2     --  C61     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N7     --  C35     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N12    --  C23     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N17    --  C105    ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N18    --  C97     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N23    --  C78     ..       0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C1     --  C9      ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C3     --  C18     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C4     --  C5      ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C14    --  C15     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C23    --  C24     ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C40    --  C41     ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C45    --  C46     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C47    --  C48     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C47    --  C50     ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C52    --  C53     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C58    --  C59     ..       0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C62    --  C63     ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C65    --  C69     ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C70    --  C71     ..       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C72    --  C73     ..       0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C73    --  C78     ..       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C99    --  C102    ..       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C106   --  C111    ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C108   --  C109    ..       0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C110   --  C111    ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C116   --  C117    ..       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C126   --  C127    ..       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C128   --  C129    ..       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C130   --  C131    ..       0.18 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        N17 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C35 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C76 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C100 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C54 Check
```

```
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C99 Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ...........        O6 Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ...........        O9 Check
PLAT369_ALERT_2_C Long    C(sp2)-C(sp2) Bond  C31    -   C32    ..      1.53 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  Hn     ..  H5AA   ..      1.95 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  Hy     ..  H4DA   ..      1.99 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H7AA   ..  H1BA   ..      1.93 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H2BA   ..  H1CA   ..      1.92 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H3BA   ..  H1EA   ..      1.99 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H7BA   ..  H3DA   ..      1.99 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H9BA   ..  H5EA   ..      1.96 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H2DA   ..  H7FA   ..      1.98 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H9DA   ..  H9EA   ..      1.99 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H0IA   ..  H6JA   ..      1.96 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N9     --  H      ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N10    --  Ha     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N4     --  Hb     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N22    --  Hc     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N3     --  He     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N16    --  Hf     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N11    --  Hg     ...    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N15    --  H4EA   ...    Please Check
```

Alert level G

```
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C264 H290 Br12 Cu6 N48 O24
           Atom count from the _atom_site data:  C264 H286 Br12 Cu6 N48 O24
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
          From the CIF: _cell_formula_units_Z    4
          From the CIF: _chemical_formula_sum  C264 H290 Br12 Cu6 N48 O24
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C       1056.00   1056.00    0.00
          H       1160.00   1144.00   16.00
          Br        48.00     48.00    0.00
          Cu        24.00     24.00    0.00
          N        192.00    192.00    0.00
          O         96.00     96.00    0.00
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............        11 Report
PLAT041_ALERT_1_G Calc. and Reported SumFormula    Strings  Differ     Please Check
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large      0.11 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large   1200.35 Why ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Br1    --  Cu4     ..       7.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Br6    --  Cu3     ..      18.8 s.u.
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   0.50) in Resd. #         2 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (   0.50) in Resd. #         3 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  O12    ..  C9      ..      2.96 Ang.
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure       ! Info
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........       142 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         2 Note
            Br
PLAT794_ALERT_5_G Tentative Bond Valency for Cu1     (II)    .....      2.02 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu3     (II)    .....      2.01 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Cu4     (II)    .....      2.08 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed          ! Info
```

```
 1 ALERT level A = Most likely a serious problem - resolve or explain
11 ALERT level B = A potentially serious problem, consider carefully
78 ALERT level C = Check. Ensure it is not caused by an omission or oversight
20 ALERT level G = General information/check it is not something unexpected

 5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
55 ALERT type 2 Indicator that the structure model may be wrong or deficient
 5 ALERT type 3 Indicator that the structure quality may be low
41 ALERT type 4 Improvement, methodology, query or suggestion
 4 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 30/03/2016; check.def file version of 30/03/2016

Datablock MOP-TO-2 - ellipsoid plot