Supporting Information

A Fluorescent Calixarene-based Dimeric Capsule Constructed by a MII-Terpyridine Interaction: Cage Structure, Inclusion Properties and Drug Release

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Materials and Instrumentation

^{1}H NMR, ^{13}C NMR, and DOSY spectra were measured on a Bruker AVANCE

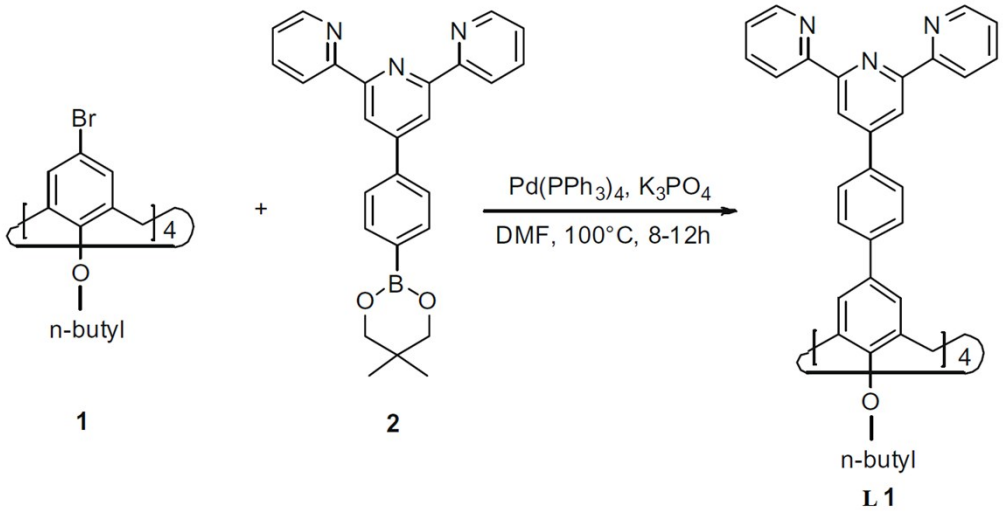
400 MHz instrument. HRESI-TOF mass spectra were measured on Bruker maXis 4G. The data analyses of ESI-TOF mass spectra were processed on Bruker Data Analysis software and the simulations were performed on Bruker Isotope Pattern software. The absorption spectra were observed with a Shimadzu UV-3600 spectrometer and fluorescence spectra were measured with an Edinburgh Instruments Ltd FLS980 spectrometer. All chemicals are of reagent grade quality obtained from commercial sources and without further purification.

Computational method

Geometry optimization of $\mathbf{Zn_4(L1)_2}$ cage and mercaptopurine@$\mathbf{Zn_4(L1)_2}$ in acetonitrile was executed at the level of B3LYP/6-31Gd with Gaussian 09.[1] Solvent effect was taken into account by using the polarizable continuum model (PCM). The complex stabilization energy (E_s) was obtained by subtracting the respective energy of cage and guest from the one of complex: E_s = E (complex) – [E (cage) + E (guest)].

Ligand Synthesis

cone-5,11,17,23-Tetra{4-(2,20:60,200-terpyridyl)-phenyl}-25,26,27,28-tetrabutoxycalix[4]arene (**L1**)



Scheme S1 The synthesis of **L1**

The synthesis process of **L1** was according to our previous publication[2]. A mixture of K_3PO_4 (1.56 g, 0.68 mmol), $Pd(PPh_3)_4$ (139 mg, 12.0 μmol), cone-5,11,17,23-tetrabromo-25,26,27,28-tetrabutoxycalix[4]arene **1**[3] (1.02 g, 1.0 mmol), and 4'-{4-(neopentylglycolatoboron) phenyl-2,20:60,200-terpyridine **2**[4] (2.86 g, 6.79

mmol) in degassed DMF (100 mL) was stirred under argon at 100 °C for 12 h. The reaction mixture was diluted with $CHCl_3$ (800 mL), and the resulting solution was washed with water (2×200 mL). The organic layer was dried with Na_2SO_4, the solvent was evaporated, and the residue was purified via dissolution in methanol (4×100 mL), leading to precipitation of the crude product as a yellow solid. After column chromatography (basic Al_2O_3; eluent: CH_2Cl_2 to CH_2Cl_2/acetone 5:1) followed by recrystallization from CH_2Cl_2/methanol 939 mg (0.5 mmol, 50%) analytically pure **L1** was obtained as colorless powder. ^{1}H NMR (400 MHz, 298 K, THF-d_8, ppm): δ 8.61 (bs, 8H), 8.46 (d, J = 4.6 Hz, 8H,), 8.43 (d, J = 8.1 Hz, 8H,), 7.70 (dd, J = 8.1 Hz, J = 7.6 Hz, 8H), 7.69 (d, J = 7.8 Hz, 8H), 7.40 (d, J = 7.8 Hz 8H), 7.21 (bs, 8H), 7.15 (dd, J = 7.6 Hz, J = 4.6 Hz, 8H), 4.70 (d, J = 13.5 Hz, 4H), 4.11 (t, J = 6.8 Hz, 8H), 3.46 (d, J = 13.5 Hz, 4H), 2.12-2.05 (m, 8H), 1.66-1.56 (m, 8H), 1.11 (t, J = 7.6 Hz, 12H). ^{13}C NMR (100 MHz, 298 K, THF-d_8, ppm): δ 156.8, 156.3, 149.8, 149.6, 142.8, 137.0, 136.9, 135.4, 127.9, 127.8, 124.1, 121.3, 118.6, 76.0, 33.4, 32.1, 20.4, 14.6. ^{1}HNMR (400 MHz, 298 K, $CDCl_3$, ppm): σ 8.53 (bs, 16H), 8.41 (d, J = 7.56Hz, 8H), 8.05 (d, J = 8.32Hz, 8H), 7.67-7.7 (m, 16H), 7.31 (bs, 8H), 7.14-7.12 (m, 8H) , 7.09 (bs, 8H), 4.64 (d, J = 13.4 Hz, 4H), 4.06 (t, J = 6.84 Hz, 8H), 3.40 (d, J = 13.7 Hz, 4H), 2.01 (m, J =7.32 Hz, 8H), 1.55 (m, J = 7.84 Hz, 8H), 1.08 (t, J = 7.56 Hz, 12H). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$, ppm): σ 156.1, 155.2, 149.3, 148.8, 141.6, 136.3, 135.9, 134.4, 127.3, 127.0, 126.9, 123.2, 121.0, 118.2, 75.2, 32.4, 31.4, 19.5, 14.1. MS (MALDI-TOF) m/z: 1878.1 [M^+].

Self-assembly of cages

1. The preparation of **$Zn_4(L1)_2(OTf)_8$** and **$Cd_4(L1)_2(OTf)_8$** by two methods:

A. **L1** (12 mg, 6.39 μmol) and $Zn(CF_3SO_3)_2$/$Cd(CF_3SO_3)_2$ (4.65 mg/5.27 mg, 12.79 μmol) were dissolved in THF (2 ml), respectively. By simply adding a THF solution of **L1** into a THF solution of $Zn(CF_3SO_3)_2$/$Cd(CF_3SO_3)_2$, cages were precipitated as a yellow amorphous solid.

B. To a mixture of $Zn(CF_3SO_3)_2$/$Cd(CF_3SO_3)_2$ (4.65 mg/5.27 mg, 12.79 μmol) and **L1** (12 mg, 6.39 μmol) acetonitrile was added. The reaction mixture was placed in an oil bath at 80 ^{0}C for 2 h and a clear solution was obtained. The cages were

obtained from diffusing hexane/THF (or ether) into the above reaction solution.

2. The preparation of **$Cd_4(L1)_2(PF_6)_8$** by anion exchange:

The counter-ions could be exchanged by adding a methanol of ammonium hexafluorophosphate (PF_6^-) to acetonitrile solution of **$Cd_4(L1)_2(OTf)_8$**. The **$Cd_4(L1)_2(PF_6)_8$** cages were obtained from diffusing hexane/THF (or ether) into the above reaction solution.

$Zn_4(L1)_2(OTf)_8$: Yield: 90 %. ^{1}H NMR (400 MHz, 298 K, CD_3CN, ppm): σ 8.80 (bs, 16H), 8.24-8.26 (m, 32H), 7.96-7.93 (m, 32H), 7.49-7.47 (bs, 16H) , 6.97 (bs, 16H), 6.59 (bs, 16H), 4.78(d, J = 12.9 Hz, 8H), 4.16 (t, J = 6.08 Hz, 16H), 3.70 (d, J = 13.2Hz, 8H), 2.22 (m, J =7.32 Hz, 16H), 1.67 (m, J = 7.84 Hz, 16H), 1.19 (t, J = 7.56 Hz, 24H). ^{13}C NMR (100 MHz, 298 K, CD_3CN, ppm): σ 158.08, 156.73, 150.00, 148.66, 143.64, 137.37, 134.77, 129.46, 128.16, 127.98, 123.64, 122.25, 120.45, 115.85, 114.91, 113.51, 77.03, 33.49, 30.58, 20.17, 14.70.

HRESI-MS m/z:

595.1986 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_1]^{7+}$calc), 595.2171 (Found);

719.3903 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_2]^{6+}$calc), 719.4120 (Found);

893.0589 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_3]^{5+}$calc), 893.0848 (Found);

1153.5618 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_4]^{4+}$calc), 1153.5941 (Found);

1587.7332 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_5]^{3+}$calc), 1587.7752 (Found);

2456.0706 ($[Zn_4C_{256}H_{216}N_{24}O_8(CF_3SO_3)_6]^{2+}$calc), 2456.1407(Found).

$Cd_4(L1)_2(OTf)_8$: Yield: 86%. ^{1}H NMR (400 MHz, 298 K, CD_3CN, ppm): σ 8.77 (s, 16H), 8.36 (d, J = 8.0 Hz, 16H), 8.18 (d, J = 8.0 Hz, 16H), 7.93 (d, J = 8.1 Hz, 16H), 7.89 (s, 16H), 7.80 (d, J = 4.2 Hz, 16H), 6.95 (t, J = 7.6 Hz, 16H), 6.69 (t, J = 6.8 Hz, 16H), 4.76 (d, J = 12.4 Hz, 8H), 4.14 (t, J = 7.6 Hz, 16H), 3.68 (d, J = 12.4 Hz, 8H), 2.28-2.20 (m, 16H), 1.71-1.62 (m, 16H), 1.18 (t, J = 7.6 Hz, 24H).

$Cd_4(L1)_2(PF_6)_8$: Yield: 80%. ^{1}H NMR (400 MHz, 298 K, CD_3CN, ppm): σ 8.74 (s, 16H), 8.33 (d, J = 8.0 Hz, 16H), 8.15 (d, J = 8.0 Hz, 16H), 7.94 (d, J = 8.0 Hz, 16H), 7.92 (s, 16H), 7.76 (d, J = 4.2 Hz, 16H), 6.89 (bs, 16H), 6.60 (bs, 16H), 4.76 (d, J = 12.4 Hz, 8H), 4.13 (t, J = 7.6 Hz, 16H), 3.68 (d, J = 12.4 Hz, 8H), 2.27-2.16 (m, 16H), 1.71-1.61 (m, 16H), 1.17 (t, J = 7.6 Hz, 24H). ^{13}C NMR (100 MHz, 298 K, CD_3CN,

ppm): σ 157.91, 155.75, 150.32, 150.23, 149.42, 143.27, 140.95, 137.38, 135.11, 129.43, 128.09, 127.85, 127.71, 124.19, 122.66, 77.02, 33.50, 30.53, 20.18, 14.70. HRESI-MS m/z:

621.6152 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_1]^{7+}$calc), 621.6106 (Found);

749.3785 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_2]^{6+}$calc), 749.3725 (Found);

928.2472 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_3]^{5+}$calc), 928.2389 (Found);

1196.5502 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_4]^{4+}$calc), 1196.5390 (Found);

1643.7218 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_5]^{3+}$ calc), 1643.7033 (Found);

2538.0605 ($[Cd_4C_{256}H_{216}N_{24}O_8(PF_6)_6]^{2+}$calc), 2538.0354 (Found).

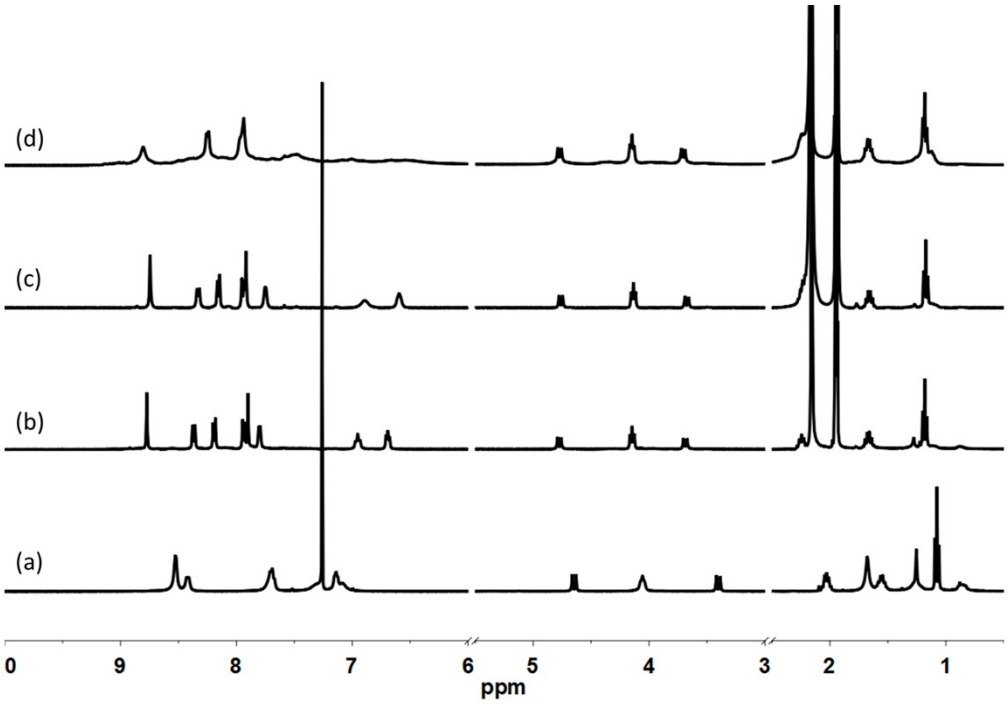


Figure S1 ^{1}H NMR spectra (400 MHz, 298 K) of (a) ligand **L1** ($CDCl_3$), (b) **$Cd_4(L1)_2(PF_6)_8$** MOC (CD_3CN), (c) **$Cd_4(L1)_2(OTf)_8$** MOC (CD_3CN), and (d) **$Zn_4(L1)_2(OTf)_8$** MOC (CD_3CN).

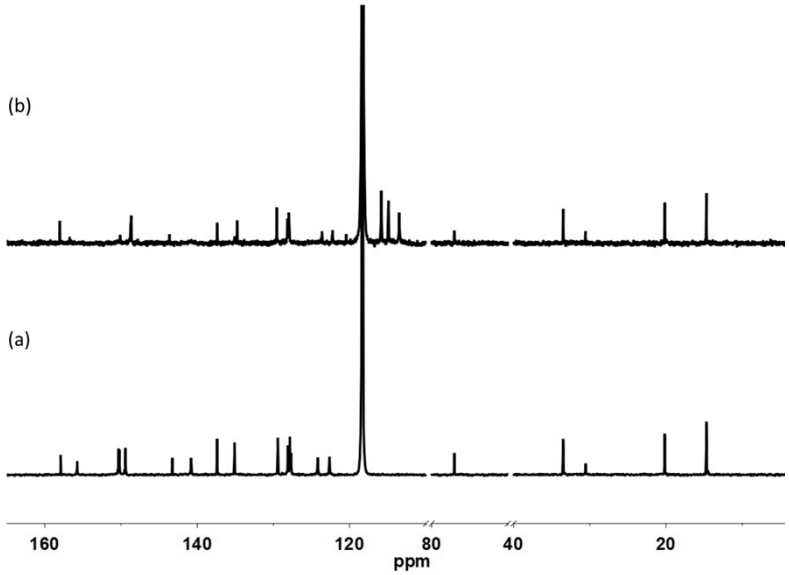


Figure S2 ^{13}C NMR spectra (100 MHz, CD_3CN, 298 K) of (a) $\mathbf{Cd_4(L1)_2(PF_6)_8}$ MOC and (b) $\mathbf{Zn_4(L1)_2(OTf)_8}$ MOC.

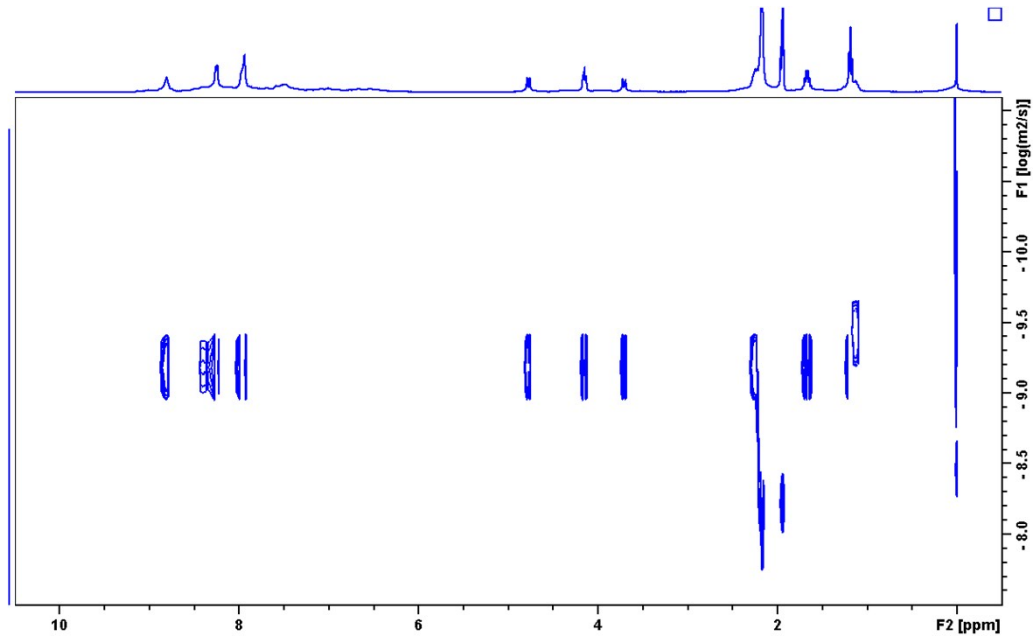


Figure S3 ^{1}H DOSY spectrum (400 MHz, CD_3CN, 298 K) of $\mathbf{Zn_4(L1)_2(OTf)_8}$ MOC.

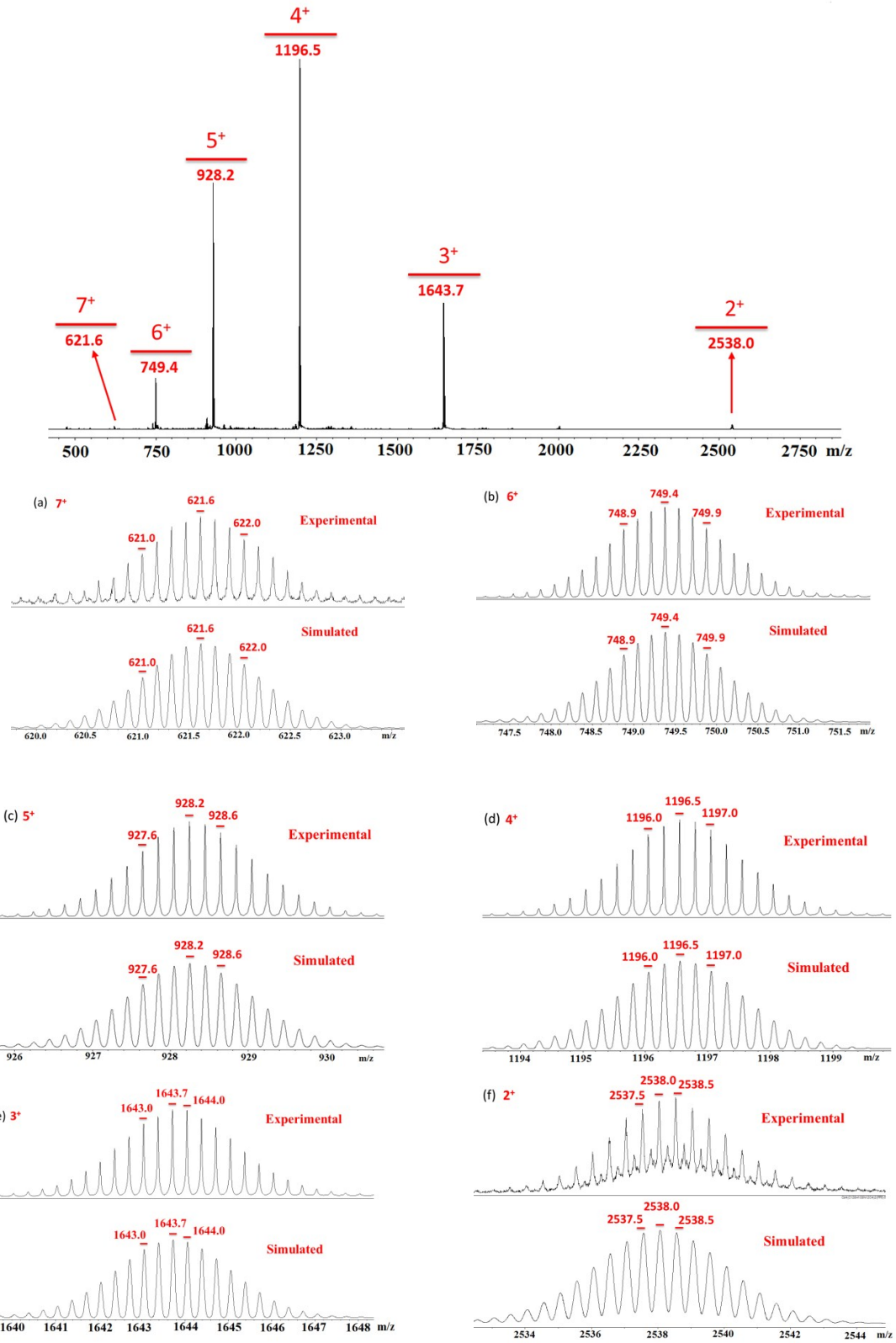


Figure S4 ESI-MS spectrum of $\mathbf{Cd_4(L1)_2(BF_6)_8}$ MOC and the isotope pattern of (a) 7^+, (b) 6^+, (c) 5^+, (d) 4^+, (e) 3^+ and (f) 2^+ peak with the corresponding simulated isotope pattern.

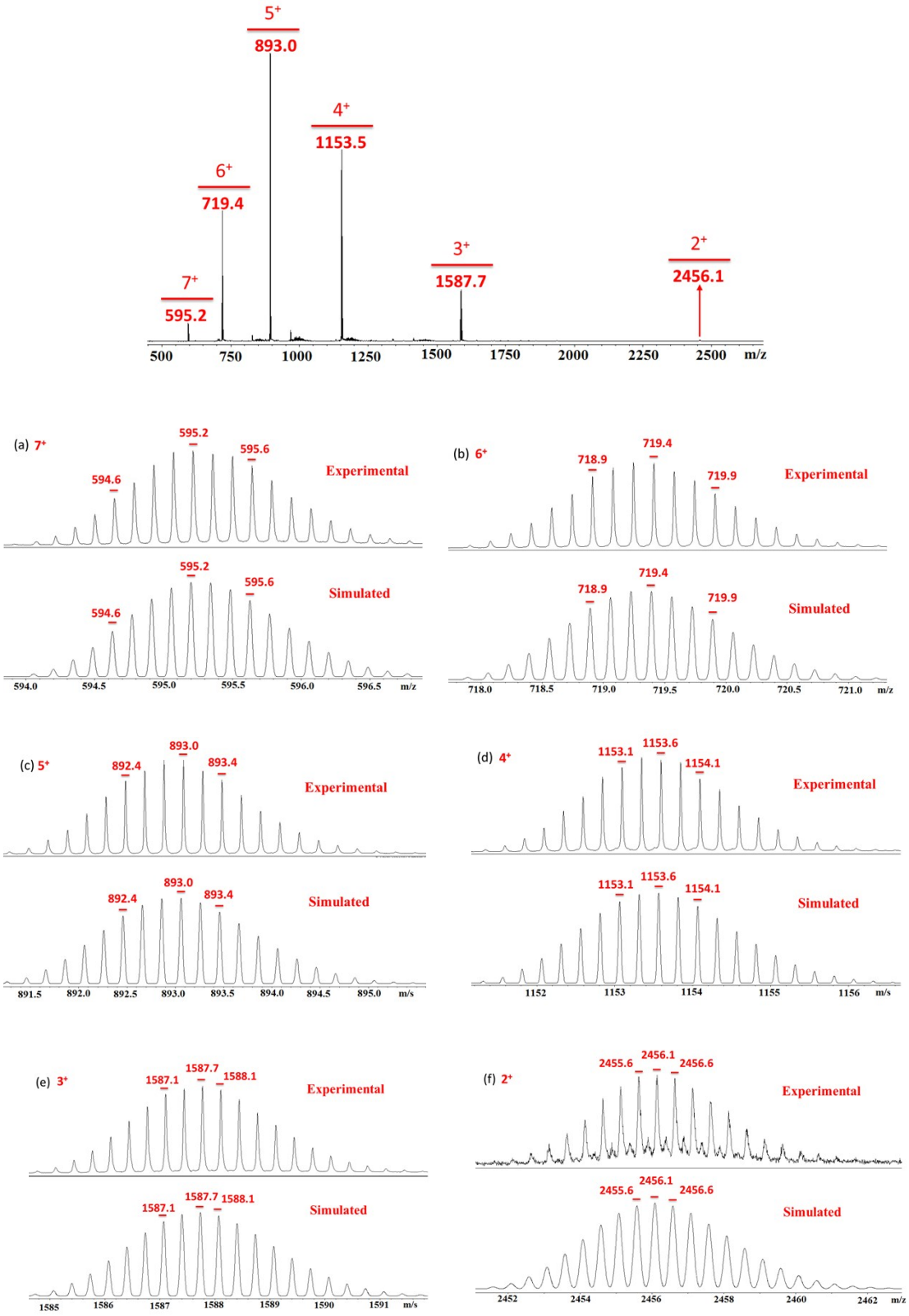


Figure S5 ESI-MS spectrum of **$Zn_4(L1)_2(OTf)_8$ MOC** and the isotope pattern of (a) 7^+, (b) 6^+, (c) 5^+, (d) 4^+, (e) 3^+ and (f) 2^+ peak with the corresponding simulated isotope pattern.

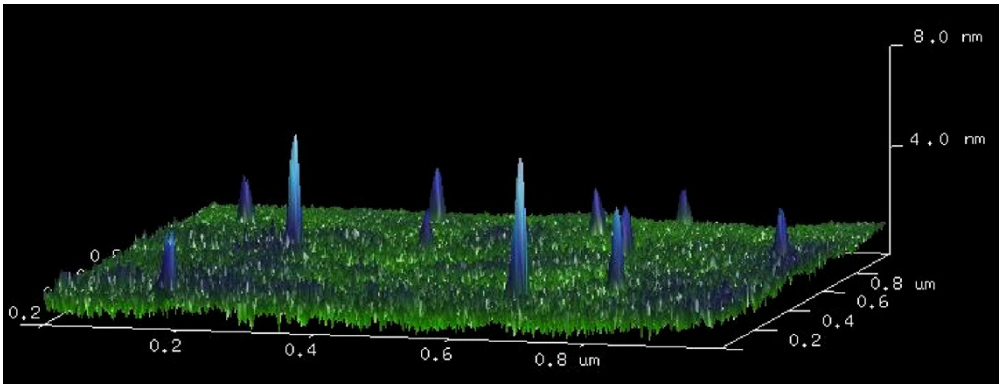


Figure S6 AFM image of **$Zn_4(L1)_2(OTf)_8$ MOC** on mica surface.

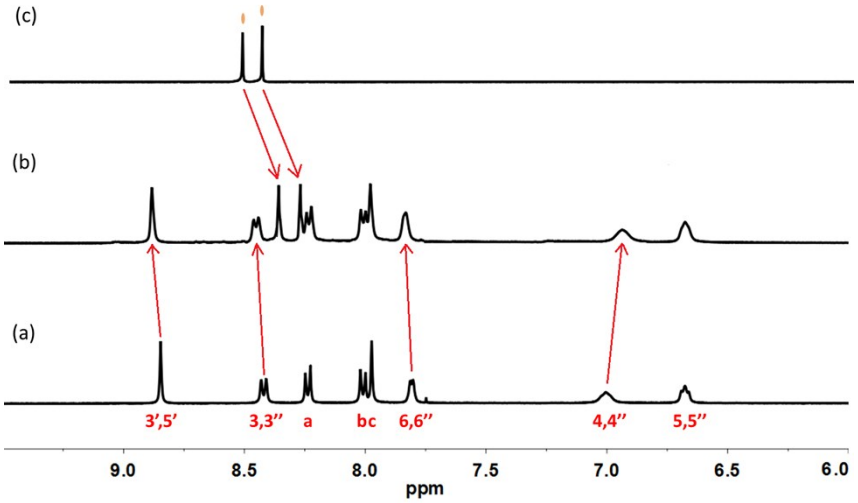


Figure S7 ^{1}H NMR (400 MHz, 298 K) (CD_3CN : D_2O = 2:1, v/v) study of (a) free **$Cd_4(L1)_2(PF_6)_8$** MOC, (b) mercaptopurine@**$Cd_4(L1)_2(PF_6)_8$** MOC system at RT, and (c) free mercaptopurine.

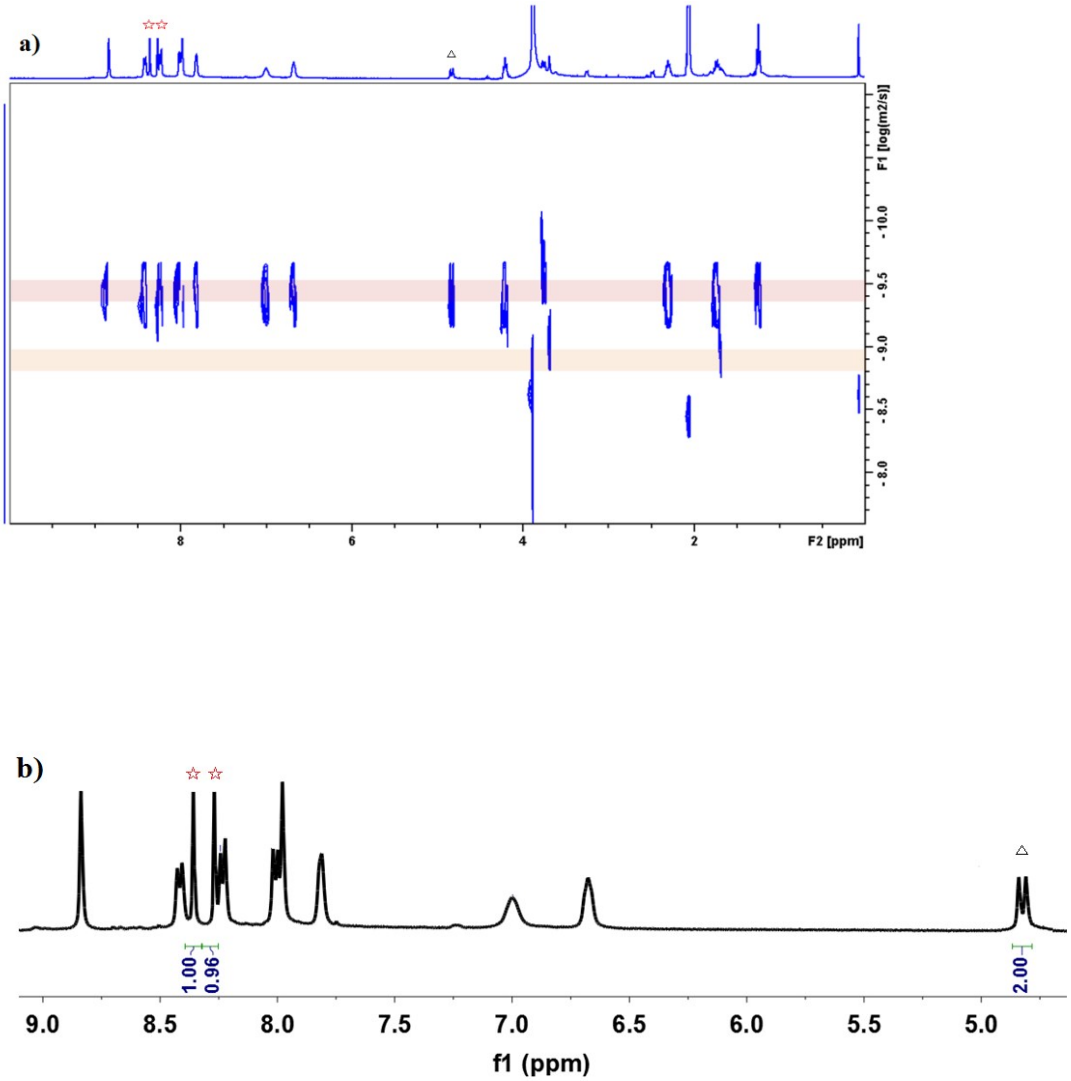
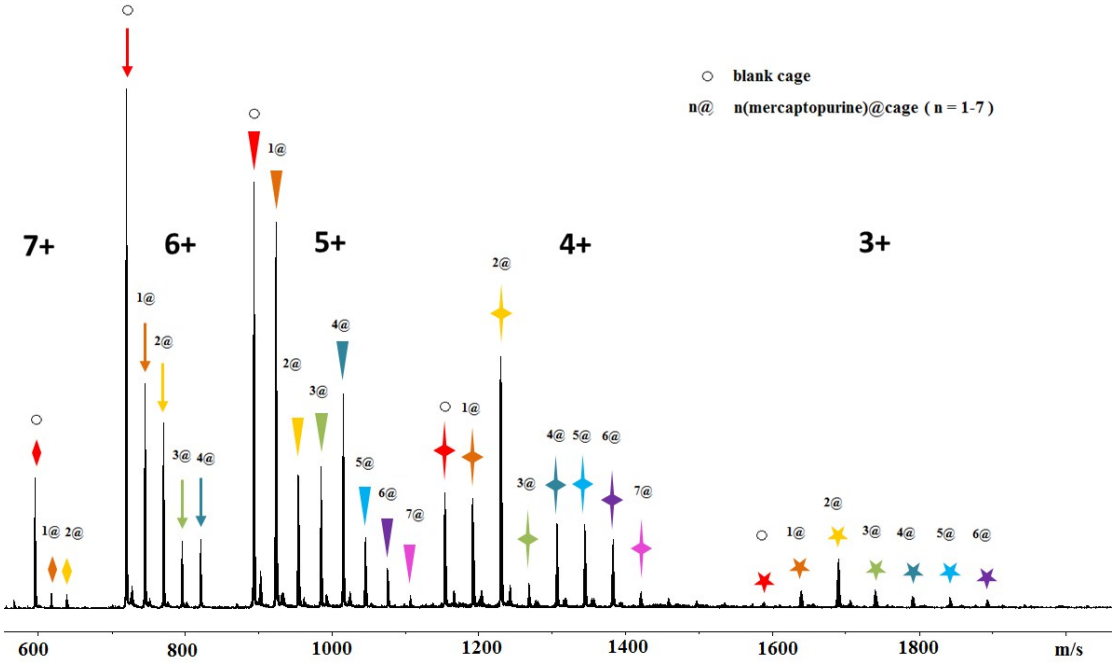
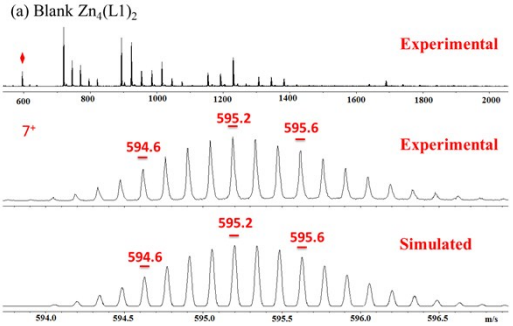
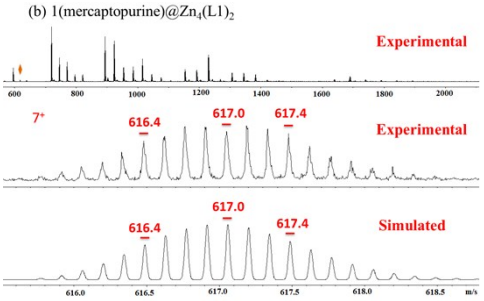
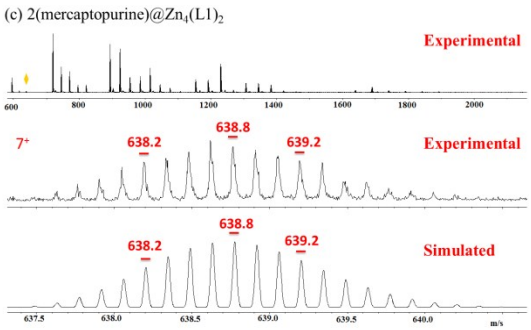


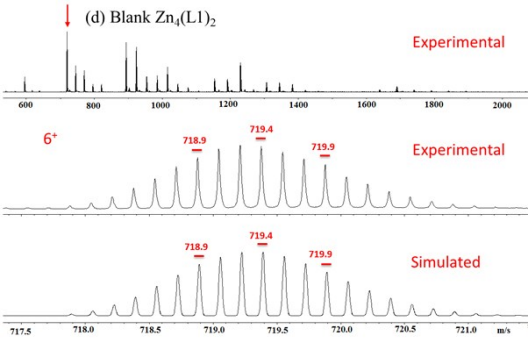
Figure S8 a) ^{1}H DOSY spectrum (400 MHz, 298 K) and b) integration of the guest peaks in ^{1}H DOSY spectrum of mercaptopurine@$Cd_4(L1)_2(PF_6)_8$ MOC system at RT in the solvent mixture of CD_3CN and D_2O (2:1 v/v). Red star: H Peaks from mercaptopurine; Black triangle: H Peaks from bridging methylene groups in calixarene.

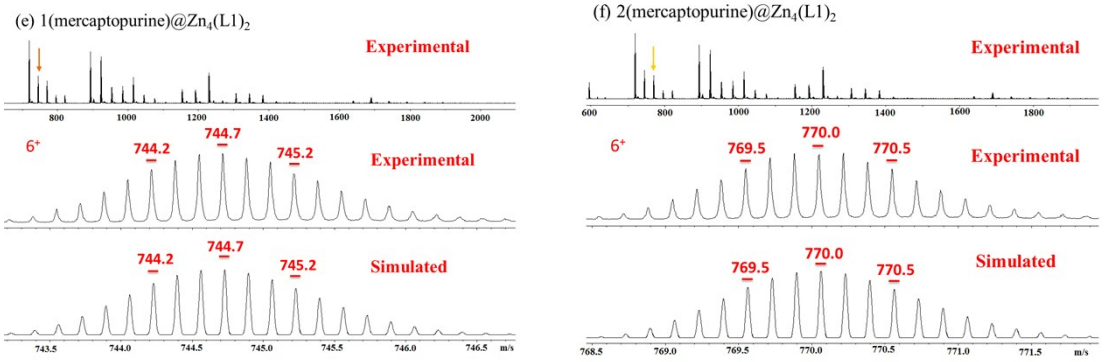

blank cage
n@ n(mercaptopurine)@cage (n = 1-7)
7+
6+
5+
4+
3+
600
800
1000
1200
1400
1600
1800
m/s


(a) Blank Zn4(L1)2
Experimental
7+
595.2
594.6
595.6
Experimental
595.2
594.6
595.6
Simulated

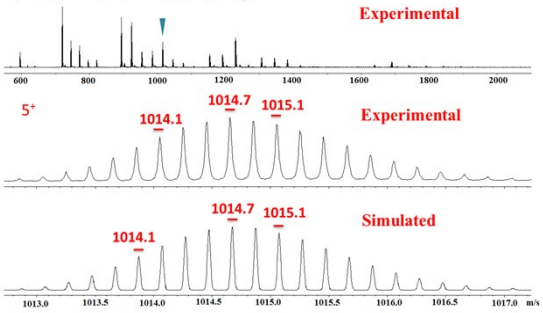

(b) 1(mercaptopurine)@Zn4(L1)2
Experimental
7+
616.4
617.0
617.4
Experimental
617.0
616.4
617.4
Simulated


(c) 2(mercaptopurine)@Zn4(L1)2
Experimental
7+
638.2
638.8
639.2
Experimental
638.8
638.2
639.2
Simulated

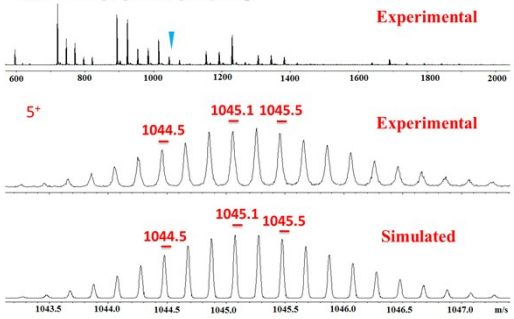

(d) Blank Zn4(L1)2
Experimental
6+
718.9
719.4
719.9
Experimental
718.9
719.4
719.9
Simulated


(e) 1(mercaptopurine)@Zn4(L1)2
Experimental
6+
744.2
744.7
745.2
Experimental
744.2
744.7
745.2
Simulated
(f) 2(mercaptopurine)@Zn4(L1)2
Experimental
6+
769.5
770.0
770.5
Experimental
769.5
770.0
770.5
Simulated
(g) 3(mercaptopurine)@Zn4(L1)2
Experimental
6+
794.9
795.4
795.9
Experimental
794.9
795.4
795.9
Simulated
(h) 4(mercaptopurine)@Zn4(L1)2
Experimental
6+
820.2
820.7
821.2
Experimental
820.2
820.7
821.2
Simulated
(i) Blank Zn4(L1)2
Experimental
5+
892.4
893.0
893.4
Experimental
892.4
893.0
893.4
Simulated
(j) 1(mercaptopurine)@Zn4(L1)2
Experimental
5+
922.8
923.4
923.8
Experimental
922.8
923.4
923.8
Simulated
(k) 2(mercaptopurine)@Zn4(L1)2
Experimental
5+
953.2
953.8
954.2
Experimental
953.2
953.8
954.2
Simulated
(l) 3(mercaptopurine)@Zn4(L1)2
Experimental
5+
983.7
984.3
984.7
Experimental
983.7
984.3
984.7
Simulated

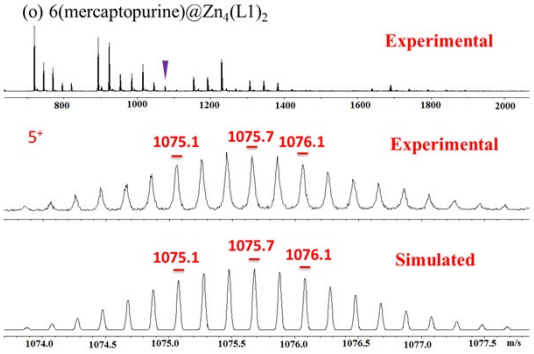
(m) 4(mercaptopurine)@$Zn_4(L1)_2$



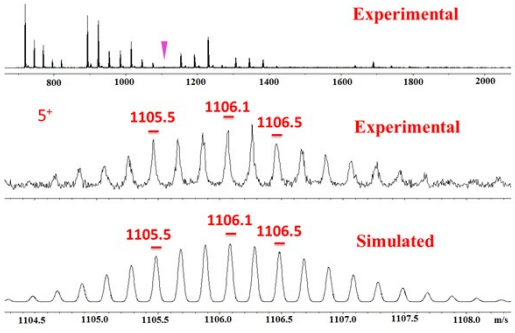
(n) 5(mercaptopurine)@$Zn_4(L1)_2$



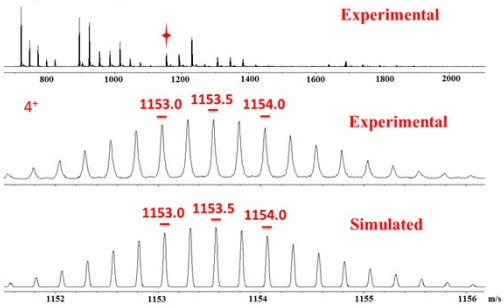
(o) 6(mercaptopurine)@$Zn_4(L1)_2$



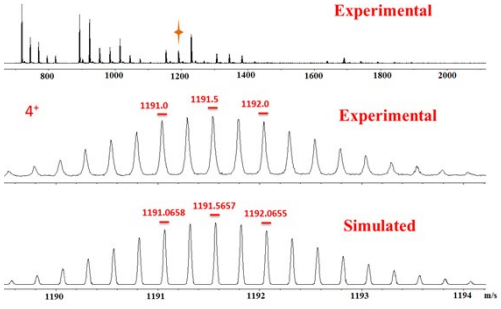
(p) 7(mercaptopurine)@$Zn_4(L1)_2$



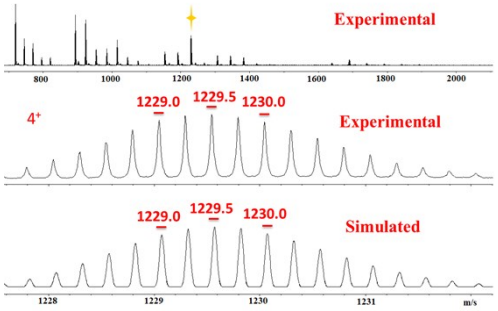
(q) Blank $Zn_4(L1)_2$



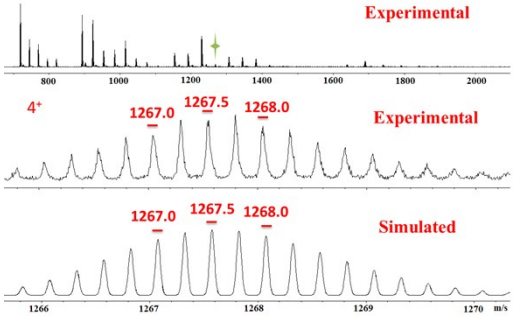
(r) 1(mercaptopurine)@$Zn_4(L1)_2$



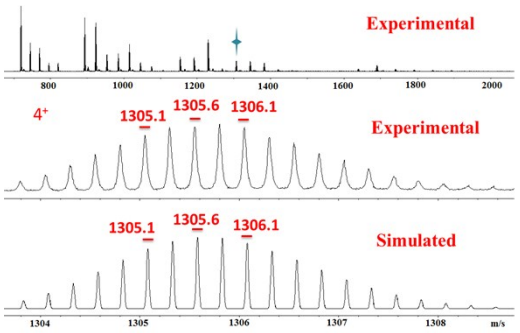
(s) 2(mercaptopurine)@$Zn_4(L1)_2$



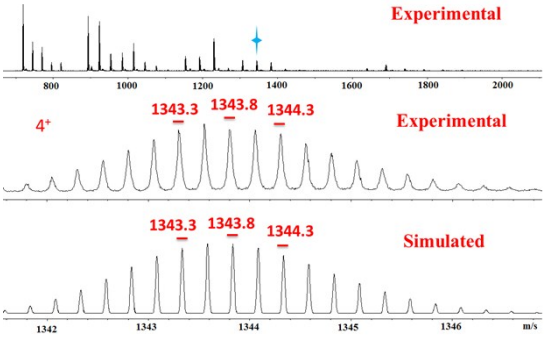
(t) 3(mercaptopurine)@$Zn_4(L1)_2$



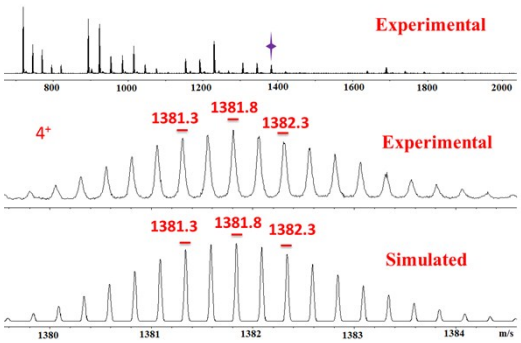
(u) 4(mercaptopurine)@$Zn_4(L1)_2$



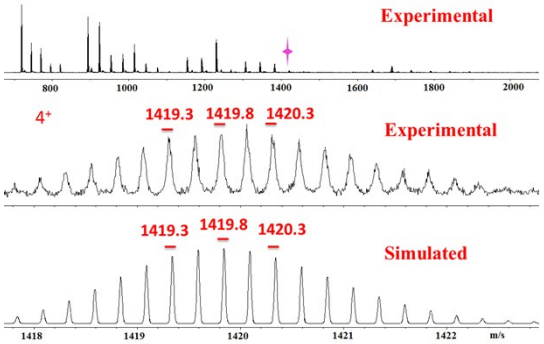
(v) 5(mercaptopurine)@$Zn_4(L1)_2$



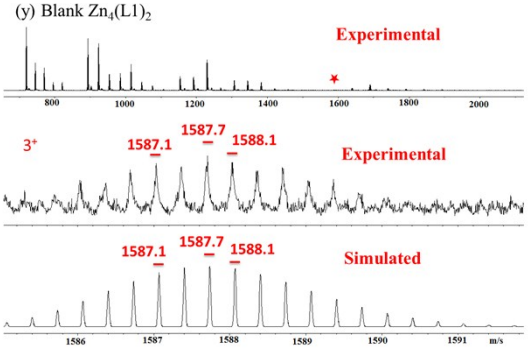
(w) 6(mercaptopurine)@$Zn_4(L1)_2$



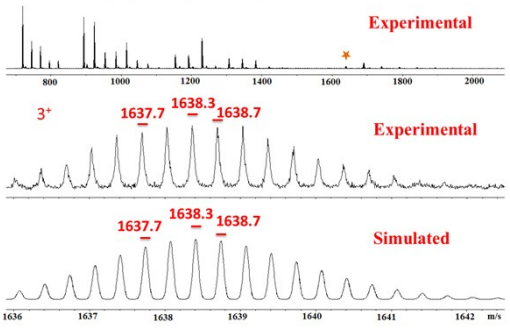
(x) 7(mercaptopurine)@$Zn_4(L1)_2$



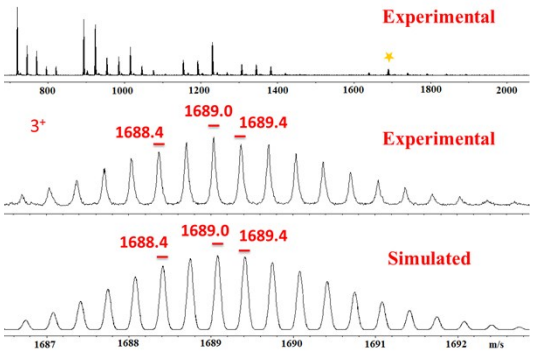
(y) Blank $Zn_4(L1)_2$



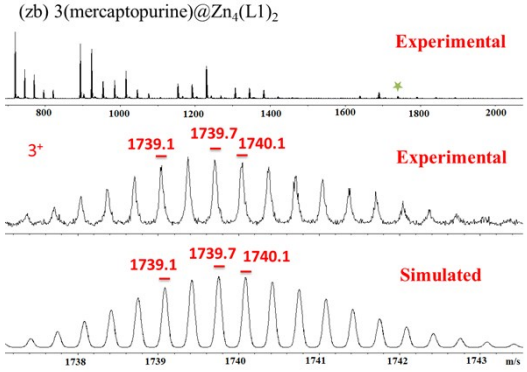
(z) 1(mercaptopurine)@$Zn_4(L1)_2$



(za) 2(mercaptopurine)@$Zn_4(L1)_2$



(zb) 3(mercaptopurine)@$Zn_4(L1)_2$



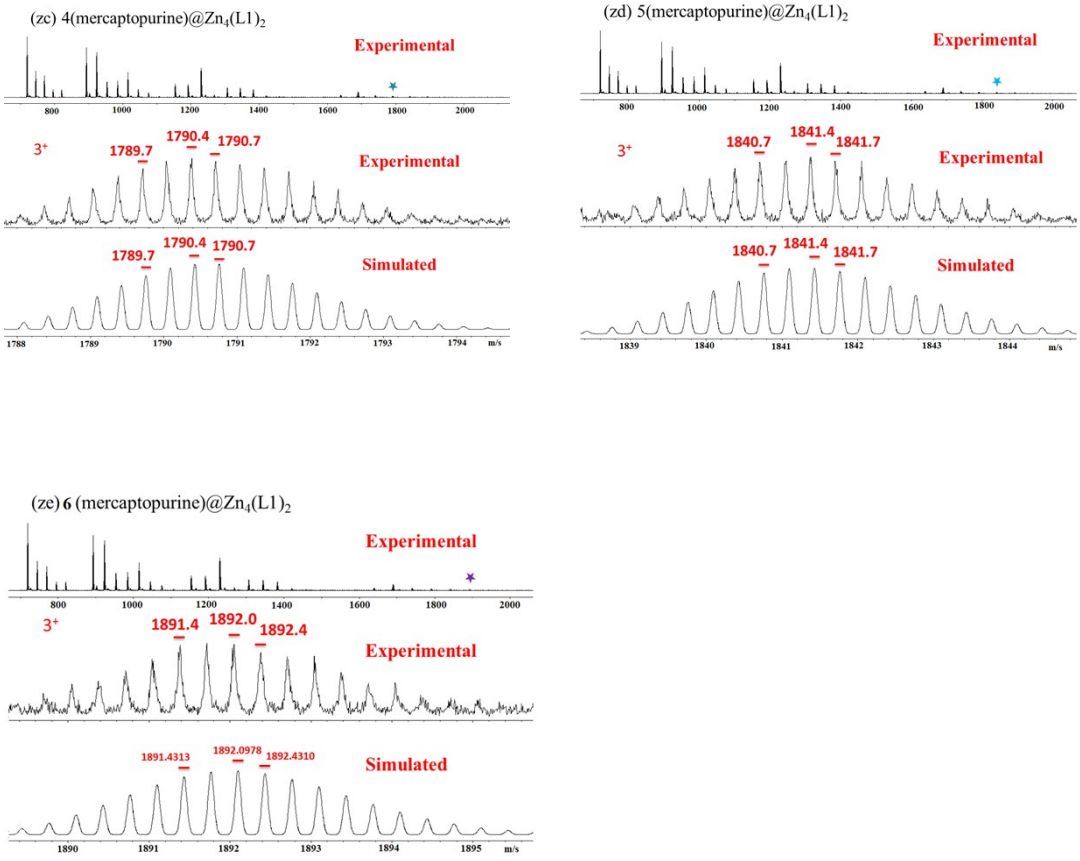
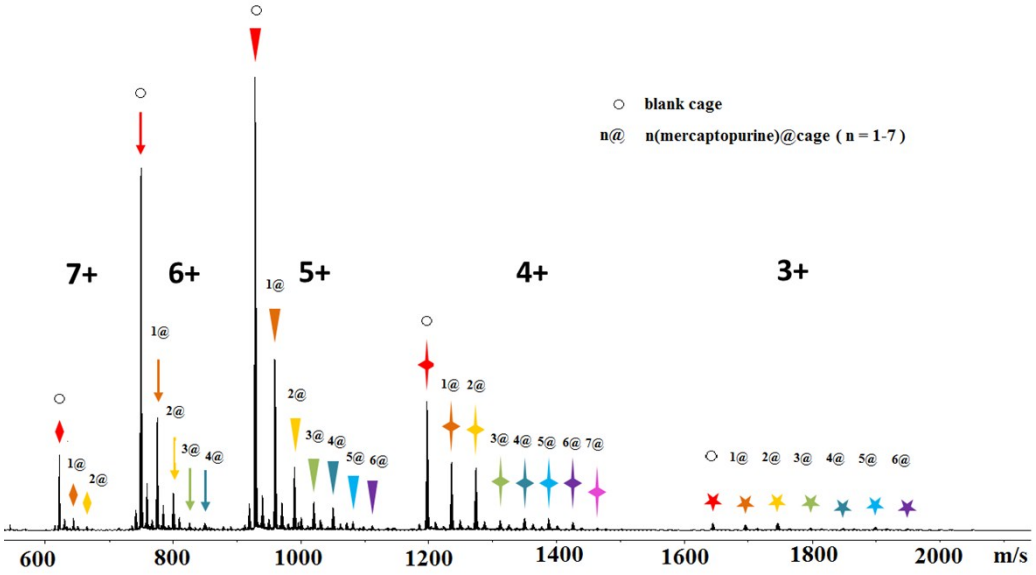
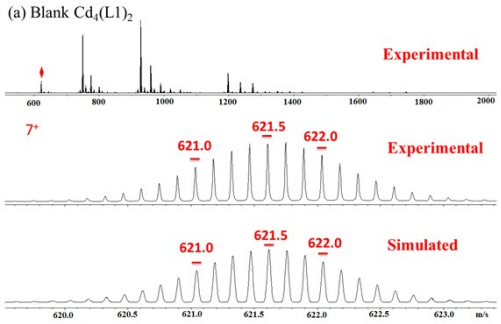
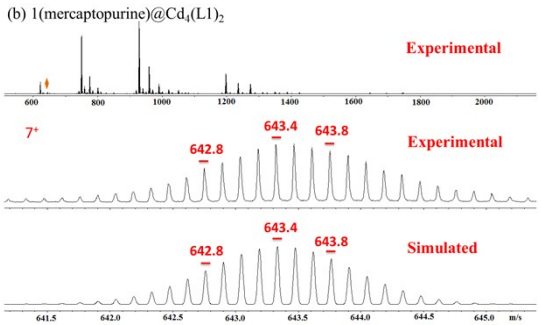
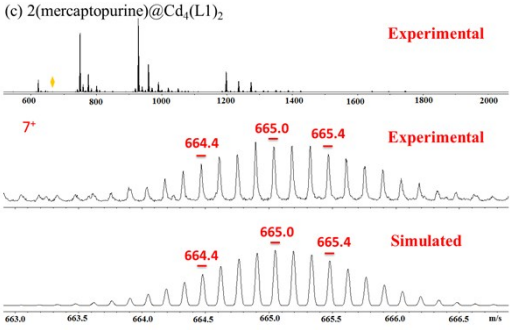


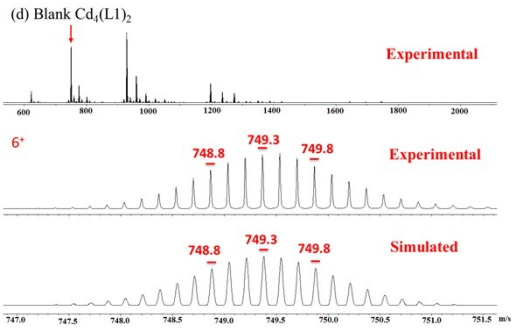
Figure S9 ESI-MS study of mercaptopurine@$\mathbf{Zn_4(L1)_2(OTf)_8}$ MOC. Rhombus, arrow, triangle, quadrangle and pentagram represent 7+, 6+, 5+, 4+, and 3+ peaks, respectively. Red, orange, gold, forestgreen, prasinous, skyblue, purple and fuchsia represent blank $\mathbf{Zn_4(L1)_2(OTf)_8}$ [(a), (d), (i), (q) and (y)], **1(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(b), (e), (j), (r) and (z)], **2(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(c), (f), (k), (s), and (za)], **3(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(g), (l), (t), and (zb)], **4(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(h), (m), (u), and (zc)], **5(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(n), (v), and (zd)], **6(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(o), (w), and (ze)], and **7(mercaptopurine)@$Zn_4(L1)_2(OTf)_8$** [(p) and (x)], respectively.

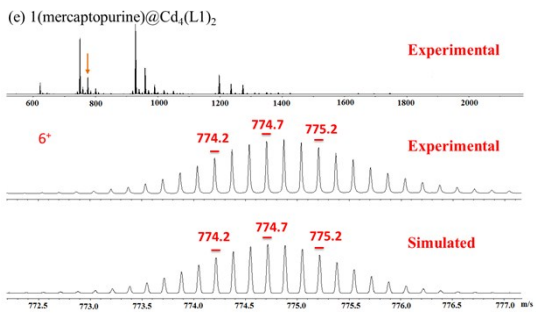

blank cage
n@ n(mercaptopurine)@cage (n = 1-7)
7+
6+
5+
4+
3+
600
800
1000
1200
1400
1600
1800
2000
m/s

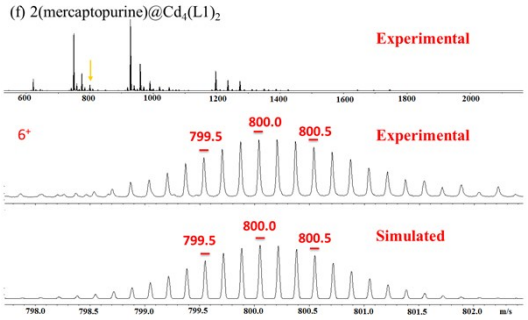

(a) Blank Cd4(L1)2
Experimental
7+
621.0
621.5
622.0
Experimental
621.0
621.5
622.0
Simulated

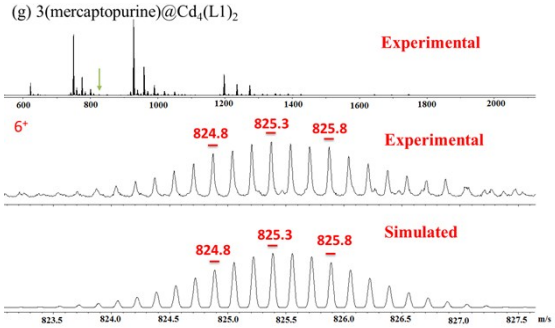

(b) 1(mercaptopurine)@Cd4(L1)2
Experimental
7+
642.8
643.4
643.8
Experimental
642.8
643.4
643.8
Simulated

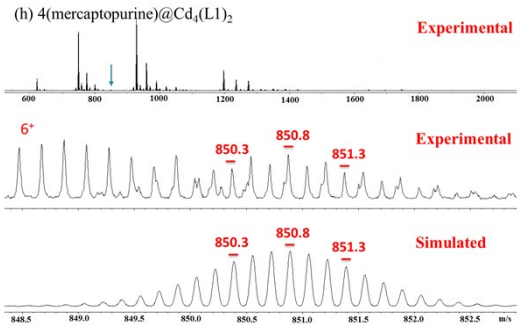

(c) 2(mercaptopurine)@Cd4(L1)2
Experimental
7+
664.4
665.0
665.4
Experimental
664.4
665.0
665.4
Simulated

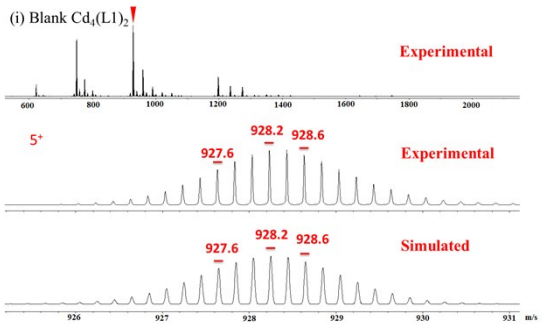

(d) Blank Cd4(L1)2
Experimental
6+
748.8
749.3
749.8
Experimental
748.8
749.3
749.8
Simulated

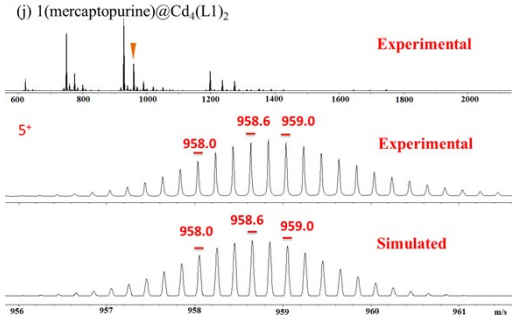

(e) 1(mercaptopurine)@Cd4(L1)2
Experimental
6+
774.2
774.7
775.2
Experimental
774.2
774.7
775.2
Simulated
m/s

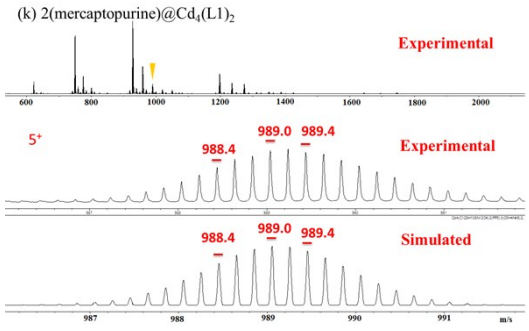

(f) 2(mercaptopurine)@Cd4(L1)2
Experimental
6+
799.5
800.0
800.5
Experimental
799.5
800.0
800.5
Simulated
m/s

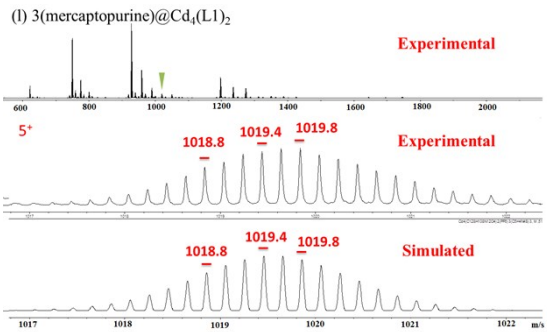

(g) 3(mercaptopurine)@Cd4(L1)2
Experimental
6+
824.8
825.3
825.8
Experimental
824.8
825.3
825.8
Simulated
m/s

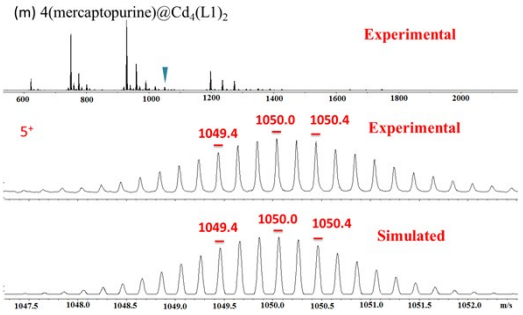

(h) 4(mercaptopurine)@Cd4(L1)2
Experimental
6+
850.3
850.8
851.3
Experimental
850.3
850.8
851.3
Simulated
m/s

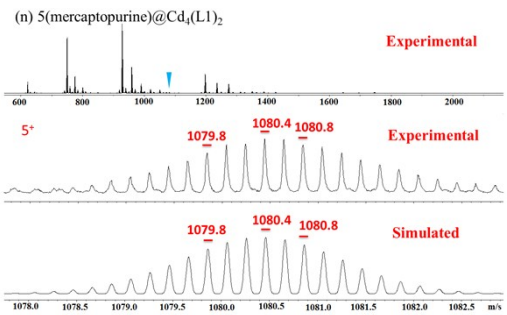

(i) Blank Cd4(L1)2
Experimental
5+
927.6
928.2
928.6
Experimental
927.6
928.2
928.6
Simulated
m/s

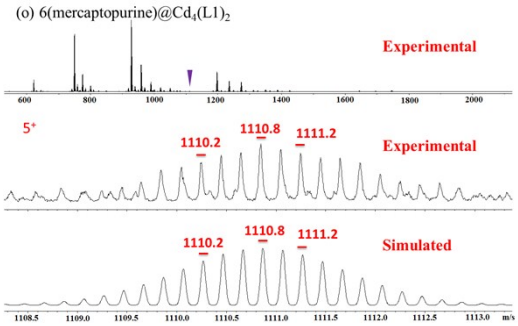

(j) 1(mercaptopurine)@Cd4(L1)2
Experimental
5+
958.0
958.6
959.0
Experimental
958.0
958.6
959.0
Simulated
m/s

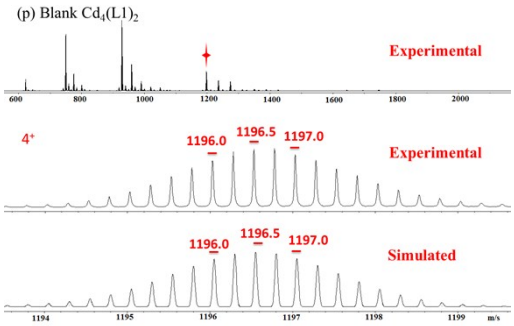

(k) 2(mercaptopurine)@Cd4(L1)2
Experimental
5+
988.4
989.0
989.4
Experimental
988.4
989.0
989.4
Simulated
m/s

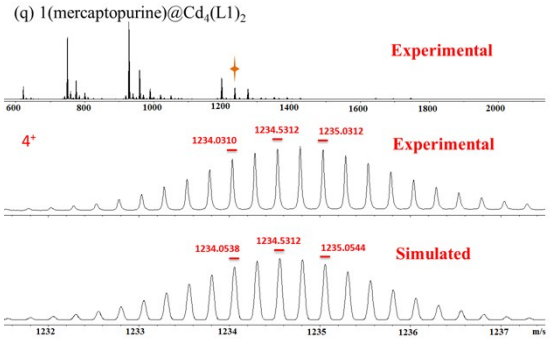

(l) 3(mercaptopurine)@Cd4(L1)2
Experimental
5+
1018.8
1019.4
1019.8
Experimental
1018.8
1019.4
1019.8
Simulated
m/s

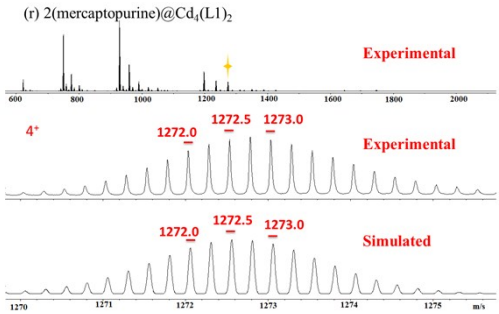

(m) 4(mercaptopurine)@Cd4(L1)2
Experimental
5+
1049.4
1050.0
1050.4
Experimental
1049.4
1050.0
1050.4
Simulated

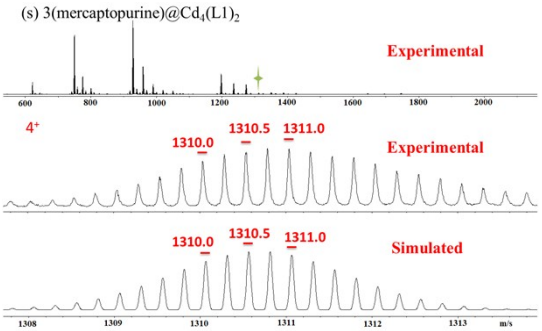

(n) 5(mercaptopurine)@Cd4(L1)2
Experimental
5+
1079.8
1080.4
1080.8
Experimental
1079.8
1080.4
1080.8
Simulated

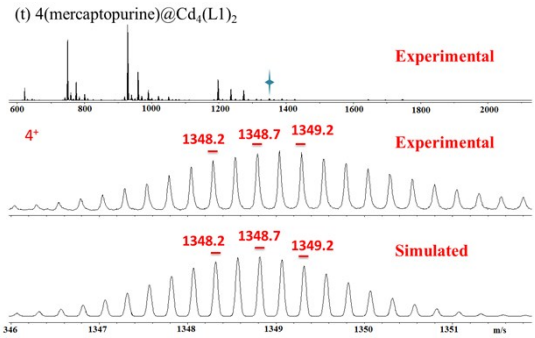

(o) 6(mercaptopurine)@Cd4(L1)2
Experimental
5+
1110.2
1110.8
1111.2
Experimental
1110.2
1110.8
1111.2
Simulated

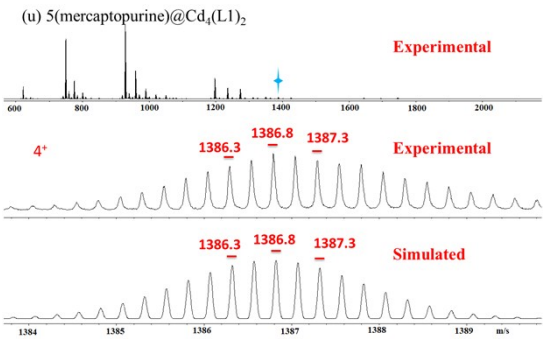

(p) Blank Cd4(L1)2
Experimental
4+
1196.0
1196.5
1197.0
Experimental
1196.0
1196.5
1197.0
Simulated

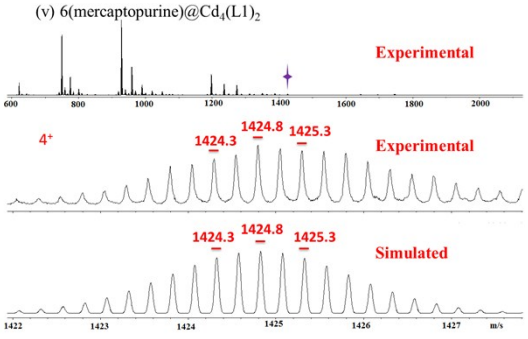

(q) 1(mercaptopurine)@Cd4(L1)2
Experimental
4+
1234.0310
1234.5312
1235.0312
Experimental
1234.0538
1234.5312
1235.0544
Simulated

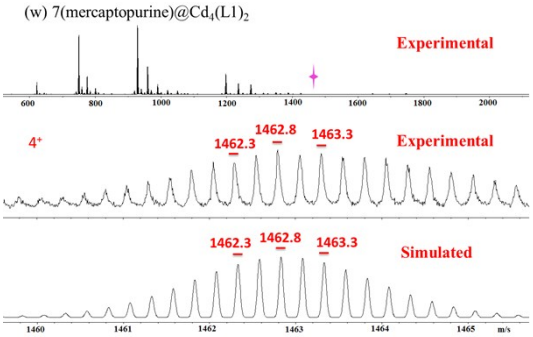

(r) 2(mercaptopurine)@Cd4(L1)2
Experimental
4+
1272.0
1272.5
1273.0
Experimental
1272.0
1272.5
1273.0
Simulated

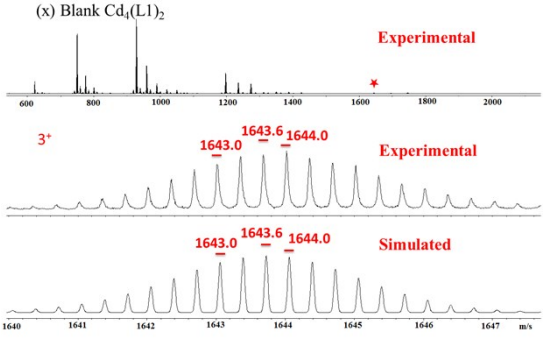

(s) 3(mercaptopurine)@Cd4(L1)2
Experimental
4+
1310.0
1310.5
1311.0
Experimental
1310.0
1310.5
1311.0
Simulated

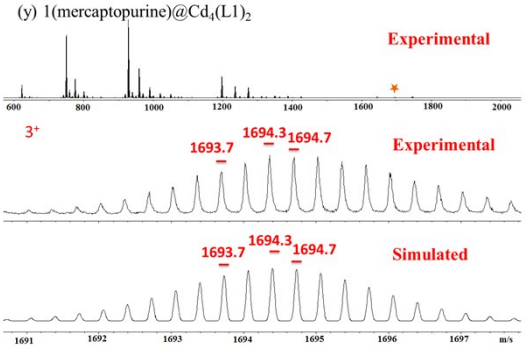

(t) 4(mercaptopurine)@Cd4(L1)2
Experimental
4+
1348.2
1348.7
1349.2
Experimental
1348.2
1348.7
1349.2
Simulated

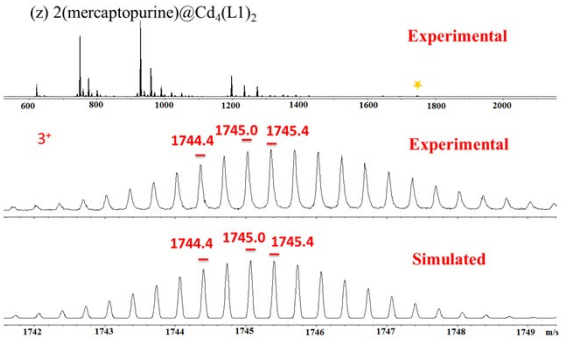

(u) 5(mercaptopurine)@Cd4(L1)2
Experimental
4+
1386.3
1386.8
1387.3
Experimental
1386.3
1386.8
1387.3
Simulated
m/s

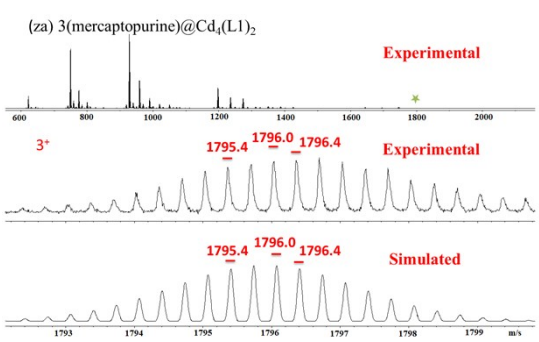

(v) 6(mercaptopurine)@Cd4(L1)2
Experimental
4+
1424.3
1424.8
1425.3
Experimental
1424.3
1424.8
1425.3
Simulated
m/s

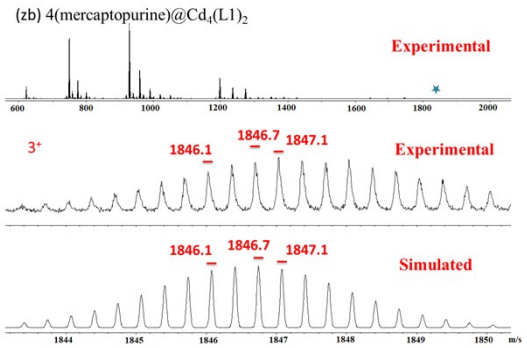

(w) 7(mercaptopurine)@Cd4(L1)2
Experimental
4+
1462.3
1462.8
1463.3
Experimental
1462.3
1462.8
1463.3
Simulated
m/s


(x) Blank Cd4(L1)2
Experimental
3+
1643.0
1643.6
1644.0
Experimental
1643.0
1643.6
1644.0
Simulated
m/s


(y) 1(mercaptopurine)@Cd4(L1)2
Experimental
3+
1693.7
1694.3
1694.7
Experimental
1693.7
1694.3
1694.7
Simulated
m/s


(z) 2(mercaptopurine)@Cd4(L1)2
Experimental
3+
1744.4
1745.0
1745.4
Experimental
1744.4
1745.0
1745.4
Simulated
m/s


(za) 3(mercaptopurine)@Cd4(L1)2
Experimental
3+
1795.4
1796.0
1796.4
Experimental
1795.4
1796.0
1796.4
Simulated
m/s


(zb) 4(mercaptopurine)@Cd4(L1)2
Experimental
3+
1846.1
1846.7
1847.1
Experimental
1846.1
1846.7
1847.1
Simulated
m/s

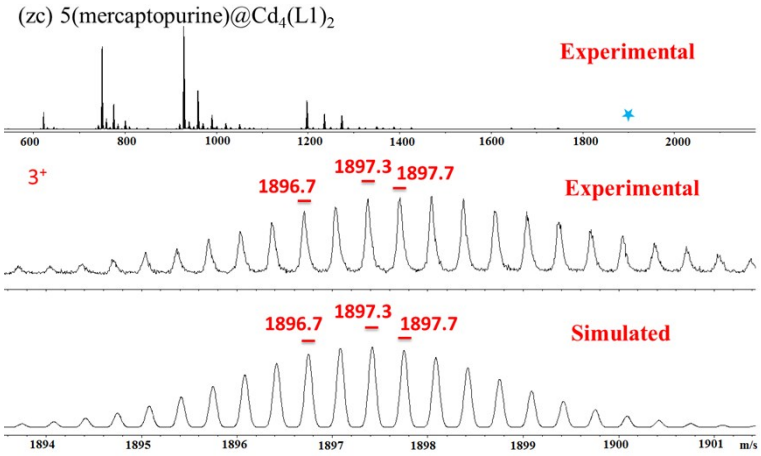


Figure S10 ESI-MS study of mercaptopurine@**$Cd_4(L1)_2(PF_6)_8$** MOC. Rhombus, arrow, triangle, quadrangle and pentagram represent 7+, 6+, 5+, 4+, and 3+ peaks, respectively. Red, orange, gold, forestgreen, prasinous, skyblue, purple and fuchsia represent blank **$Cd_4(L1)_2(PF_6)_8$** [(a), (d), (i), (p) and (x)], **1(mercaptopurine)@$Cd_4(L1)_2(PF_6)_8$** [(b), (e), (j), (q) and (y)], **2(mercaptopurine)@ $Cd_4(L1)_2(PF_6)_8$** [(c), (f), (k), (r), and (z)], **3(mercaptopurine)@$Cd_4(L1)_2(PF_6)_8$** [(g), (l), (s), and (za)], **4(mercaptopurine)@$Cd_4(L1)_2(PF_6)_8$** [(h), (m), (t), and (zb)], **5(mercaptopurine)@ $Cd_4(L1)_2(PF_6)_8$** [(m), (u), and (zc)], **6(mercaptopurine)@$Cd_4(L1)_2(PF_6)_8$** [(o) and (v)], and **7(mercaptopurine)@$Cd_4(L1)_2(PF_6)_8$** [(w)], respectively.

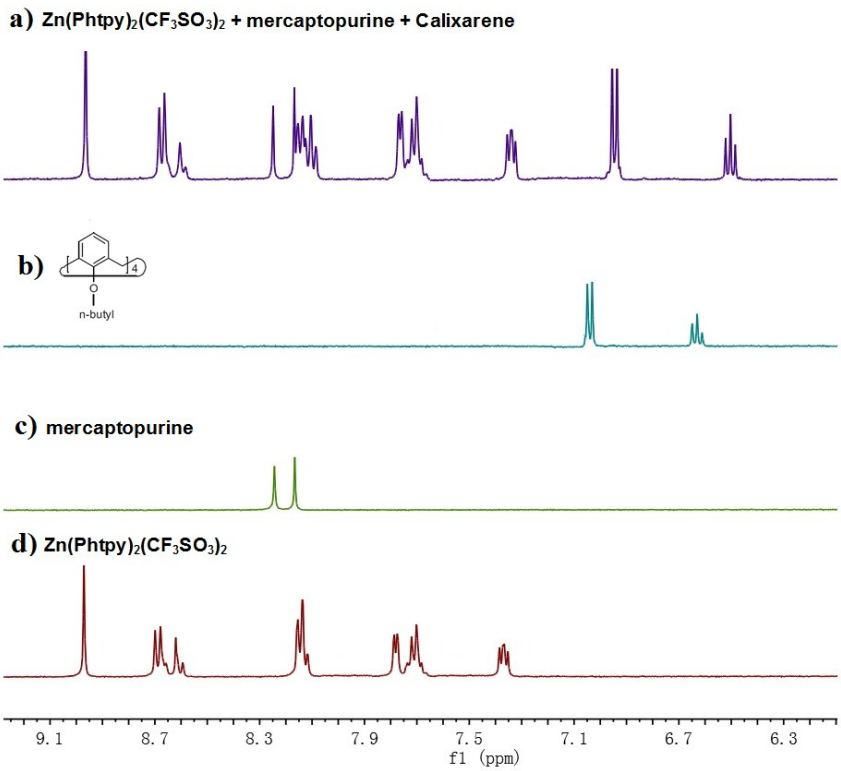


Figure S11 ^{1}H NMR spectra (400 MHz, 298 K) of a) the mixture, b) 25,26,27,28-tetrabutoxycalix[4]arene, c) mercaptopurine, and d) Zn(phenyl-tpy)$_2$(CF$_3$SO$_3$)$_2$ in CD$_3$CN and D$_2$O (v:v = 2:1).

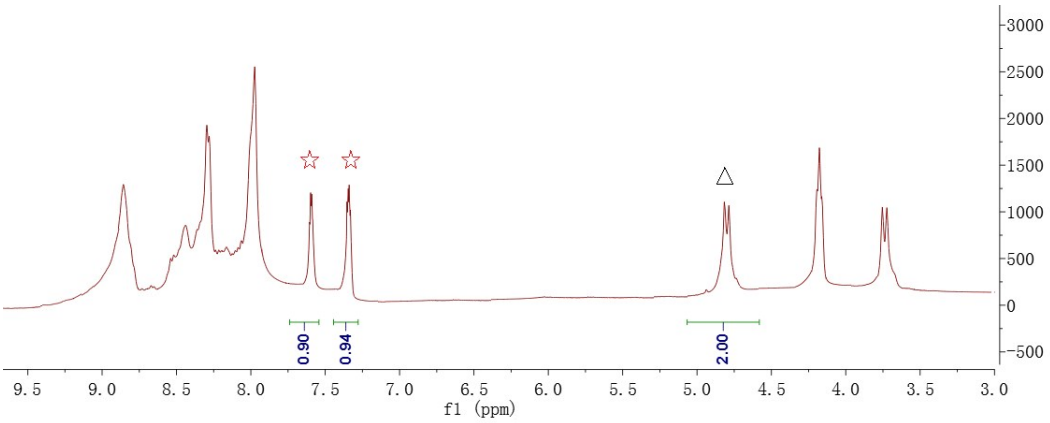


Figure S 12 ^{1}H NMR of mercaptopurine@**Zn$_4$L$_2$** cages. Red star: H Peaks from mercaptopurine; Black triangle: H Peaks from bridging methylene groups in calixarene.

Table S1. Cartesian coordinates of $\mathbf{Zn_4L_2}$ cages from B3LYP/6-31Gd optimization.

atom	x	y	z		atom	x	y	z
C(1)	1.015	6.184	-8.789		C(41)	11.668	-2.993	1.670
C(2)	2.610	5.018	-7.551		C(42)	12.354	-3.760	0.540
C(3)	2.851	4.139	-6.373		C(43)	11.832	-3.343	-0.834
C(4)	3.626	5.467	-8.399		C(44)	12.097	3.336	-0.338
C(5)	3.302	6.300	-9.468		C(45)	10.446	2.103	3.462
N(6)	1.325	5.377	-7.762		C(46)	10.140	-3.534	-2.599
C(7)	1.975	6.671	-9.669		C(47)	12.508	-0.653	-3.505
C(8)	4.134	3.763	-5.979		C(48)	10.810	-2.524	-3.309
C(9)	3.162	2.578	-4.146		C(49)	12.466	-2.328	-1.575
C(10)	4.315	2.984	-4.828		C(50)	11.941	-1.883	-2.802
N(11)	1.752	3.745	-5.689		C(51)	14.564	1.926	-2.927
C(12)	1.900	2.962	-4.603		C(52)	14.674	3.449	-2.987
N(13)	-0.398	3.364	-4.026		C(53)	14.557	1.598	1.964
C(14)	-1.517	3.065	-3.354		C(54)	15.228	2.875	1.458
C(15)	0.632	1.410	-3.073		C(55)	14.841	-2.268	-1.516
C(16)	0.668	2.559	-3.874		C(56)	15.962	-1.432	-0.914
C(17)	-1.637	1.957	-2.515		C(57)	14.497	-2.719	2.815
C(18)	-0.541	1.106	-2.385		C(58)	14.762	-2.498	4.305
C(19)	12.114	0.228	3.731		C(59)	15.577	3.945	-4.130
C(20)	11.592	1.457	2.993		C(60)	15.691	-1.322	4.650
O(21)	13.589	-1.717	-1.064		C(61)	17.370	-1.937	-1.268
O(22)	13.307	1.304	1.302		C(62)	6.709	2.323	-5.219
C(23)	12.348	1.518	-2.132		C(63)	7.983	2.033	-4.743
O(24)	13.648	-1.704	2.222		C(64)	5.947	2.658	-2.955
C(25)	9.826	3.147	2.755		C(65)	5.667	2.642	-4.332
C(26)	10.401	3.527	1.531		C(66)	8.276	2.075	-3.368
C(27)	11.560	2.928	1.030		C(67)	7.228	2.392	-2.484
C(28)	11.548	2.469	-1.467		C(68)	0.668	9.878	3.594
C(29)	10.212	2.605	-1.855		C(69)	2.557	8.575	3.964
C(30)	9.654	1.826	-2.878		C(70)	3.057	7.212	4.290
C(31)	10.444	0.807	-3.430		C(71)	3.392	9.671	3.742
C(32)	11.769	0.603	-3.039		C(72)	2.822	10.906	3.434
C(33)	9.614	-2.576	2.945		N(73)	1.211	8.690	3.895
C(34)	10.205	-1.407	3.449		C(74)	1.436	11.015	3.355
C(35)	11.532	-1.067	3.172		C(75)	4.379	6.800	4.119
C(36)	10.356	-3.322	2.016		C(76)	3.724	4.622	4.878
C(37)	12.175	1.912	1.792		C(77)	4.733	5.459	4.366
C(38)	10.673	-3.922	-1.359		N(78)	2.110	6.366	4.724
O(39)	13.701	1.463	-1.864		C(79)	2.435	5.112	5.066
C(40)	12.293	-1.926	2.355		N(80)	0.081	4.825	5.438

atom	x	y	z		atom	x	y	z
C(81)	-0.967	4.178	5.961		C(121)	1.001	-10.576	-3.166
C(82)	1.526	3.148	6.373		C(122)	4.396	-6.725	-3.964
C(83)	1.316	4.316	5.635		C(123)	3.998	-4.513	-4.799
C(84)	-0.846	3.009	6.710		C(124)	4.897	-5.438	-4.240
C(85)	0.428	2.488	6.921		N(125)	2.213	-6.080	-4.685
C(86)	6.955	5.610	3.185		C(126)	2.675	-4.873	-5.038
C(87)	8.173	5.058	2.804		C(127)	-0.561	-3.662	-6.181
C(88)	6.504	3.677	4.533		C(128)	2.026	-2.806	-6.348
C(89)	6.077	4.926	4.047		C(129)	1.671	-3.977	-5.672
C(90)	8.576	3.783	3.243		C(130)	-0.294	-2.485	-6.879
C(91)	7.713	3.119	4.136		C(131)	1.026	-2.050	-6.958
C(92)	0.506	-4.410	9.453		C(132)	7.078	-5.767	-3.005
C(93)	2.365	-4.533	8.066		C(133)	8.339	-5.318	-2.625
C(94)	2.833	-4.674	6.662		C(134)	6.827	-3.848	-4.426
C(95)	3.225	-4.388	9.155		C(135)	6.281	-5.034	-3.905
C(96)	2.683	-4.247	10.432		C(136)	8.859	-4.097	-3.097
C(97)	1.299	-4.252	10.587		C(137)	8.071	-3.386	-4.022
C(98)	4.124	-4.368	6.238		C(138)	17.059	3.579	-3.975
C(99)	3.439	-4.886	3.997		C(139)	17.151	-1.535	4.233
C(100)	4.441	-4.423	4.868		C(140)	17.733	-1.823	-2.754
N(101)	1.887	-5.071	5.797		C(141)	16.560	3.175	2.167
C(102)	2.182	-5.225	4.498		C(142)	17.683	2.175	1.862
N(103)	-0.156	-5.701	4.238		N(143)	0.390	-4.392	-5.589
C(104)	-1.199	-6.194	3.560		N(144)	1.023	-4.550	8.224
C(105)	1.268	-6.304	2.399		H(145)	-0.034	6.439	-8.897
C(106)	1.067	-5.749	3.665		H(146)	4.656	5.176	-8.240
C(107)	-1.085	-6.761	2.291		H(147)	4.083	6.655	-10.132
C(108)	0.175	-6.817	1.703		H(148)	1.683	7.321	-10.486
C(109)	6.537	-3.064	5.117		H(149)	5.000	4.116	-6.522
C(110)	7.767	-2.617	4.651		H(150)	3.248	1.974	-3.252
C(111)	6.263	-4.381	3.125		H(151)	-2.354	3.742	-3.491
C(112)	5.756	-3.964	4.369		H(152)	1.490	0.752	-3.003
C(113)	8.277	-3.029	3.405		H(153)	-2.569	1.767	-1.994
C(114)	7.485	-3.916	2.652		H(154)	-0.596	0.218	-1.764
C(115)	0.365	-9.379	-3.483		H(155)	13.199	0.169	3.680
C(116)	2.393	-8.292	-3.821		H(156)	11.842	0.318	4.789
C(117)	3.045	-7.002	-4.176		H(157)	9.929	4.302	0.933
C(118)	3.101	-9.457	-3.520		H(158)	9.609	3.378	-1.388
C(119)	2.394	-10.612	-3.190		H(159)	10.001	0.137	-4.160
N(120)	1.041	-8.267	-3.807		H(160)	9.628	-0.748	4.091

atom	x	y	z		atom	x	y	z
H(161)	9.916	-4.207	1.568		H(201)	5.119	7.504	3.764
H(162)	10.164	-4.681	-0.772		H(202)	3.926	3.577	5.073
H(163)	13.430	-3.601	0.578		H(203)	-1.944	4.613	5.780
H(164)	12.174	-4.833	0.671		H(204)	2.529	2.775	6.545
H(165)	13.182	3.281	-0.345		H(205)	-1.730	2.532	7.118
H(166)	11.812	4.378	-0.521		H(206)	0.570	1.587	7.509
H(167)	10.036	1.781	4.415		H(207)	6.684	6.575	2.772
H(168)	13.571	-0.556	-3.291		H(208)	8.816	5.636	2.148
H(169)	12.393	-0.771	-4.589		H(209)	5.891	3.116	5.231
H(170)	10.445	-2.221	-4.284		H(210)	7.968	2.134	4.509
H(171)	15.532	1.466	-2.715		H(211)	-0.577	-4.429	9.523
H(172)	14.209	1.538	-3.891		H(212)	4.300	-4.400	9.018
H(173)	15.057	3.820	-2.027		H(213)	3.337	-4.137	11.290
H(174)	13.669	3.870	-3.114		H(214)	0.837	-4.143	11.562
H(175)	15.177	0.720	1.773		H(215)	4.871	-4.059	6.956
H(176)	14.397	1.674	3.046		H(216)	3.621	-4.930	2.931
H(177)	15.392	2.787	0.377		H(217)	-2.165	-6.137	4.049
H(178)	14.543	3.718	1.616		H(218)	2.261	-6.359	1.970
H(179)	14.919	-3.318	-1.197		H(219)	-1.964	-7.150	1.790
H(180)	14.869	-2.254	-2.614		H(220)	0.313	-7.260	0.722
H(181)	15.832	-1.432	0.175		H(221)	6.180	-2.687	6.070
H(182)	15.838	-0.393	-1.245		H(222)	8.347	-1.949	5.279
H(183)	15.425	-2.686	2.237		H(223)	5.710	-5.091	2.519
H(184)	14.043	-3.705	2.667		H(224)	7.821	-4.251	1.676
H(185)	13.798	-2.380	4.817		H(225)	-0.717	-9.300	-3.485
H(186)	15.202	-3.428	4.694		H(226)	4.183	-9.473	-3.554
H(187)	15.483	5.037	-4.190		H(227)	2.929	-11.527	-2.957
H(188)	15.200	3.555	-5.086		H(228)	0.415	-11.452	-2.912
H(189)	15.310	-0.404	4.187		H(229)	5.043	-7.489	-3.556
H(190)	15.650	-1.156	5.734		H(230)	4.315	-3.500	-5.002
H(191)	17.477	-2.981	-0.942		H(231)	-1.578	-4.031	-6.091
H(192)	18.095	-1.360	-0.679		H(232)	3.061	-2.496	-6.423
H(193)	6.519	2.283	-6.288		H(233)	-1.102	-1.934	-7.347
H(194)	8.773	1.799	-5.451		H(234)	1.280	-1.141	-7.492
H(195)	5.165	2.914	-2.245		H(235)	6.709	-6.686	-2.562
H(196)	7.417	2.418	-1.415		H(236)	8.917	-5.923	-1.934
H(197)	-0.416	9.912	3.549		H(237)	6.276	-3.259	-5.151
H(198)	4.468	9.573	3.818		H(238)	8.412	-2.435	-4.411
H(199)	3.457	11.769	3.262		H(239)	17.656	4.022	-4.780
H(200)	0.953	11.956	3.117		H(240)	17.222	2.496	-4.003

atom	x	y	z		atom	x	y	z
H(241)	17.456	3.950	-3.022		C(281)	-0.166	-0.140	4.440
H(242)	17.771	-0.683	4.531		N(282)	-0.020	-2.672	5.603
H(243)	17.255	-1.651	3.147		C(283)	1.063	-0.674	4.818
H(244)	17.568	-2.434	4.704		C(284)	-3.692	-2.675	5.136
H(245)	18.773	-2.125	-2.926		C(285)	-4.466	-4.707	6.149
H(246)	17.623	-0.790	-3.108		C(286)	-4.764	-3.523	5.453
H(247)	17.100	-2.458	-3.383		N(287)	-2.141	-4.153	6.171
H(248)	16.887	4.179	1.867		C(288)	-3.142	-4.991	6.488
H(249)	16.394	3.222	3.252		N(289)	-1.377	-6.409	7.286
H(250)	17.449	1.167	2.224		C(290)	-0.901	-7.494	7.913
H(251)	18.621	2.484	2.338		C(291)	-3.608	-7.138	7.763
H(252)	17.865	2.106	0.782		C(292)	-2.714	-6.224	7.203
C(253)	1.503	-4.899	-1.744		C(293)	-1.730	-8.453	8.489
C(254)	-0.757	-4.516	-2.039		C(294)	-3.109	-8.266	8.412
C(255)	-1.979	-4.866	-2.811		C(295)	-6.516	-1.824	4.902
C(256)	-0.760	-3.572	-1.008		C(296)	-7.771	-1.475	4.421
C(257)	0.428	-3.291	-0.339		C(297)	-7.089	-4.154	4.708
N(258)	0.369	-5.165	-2.405		C(298)	-6.138	-3.172	5.034
C(259)	1.586	-3.970	-0.709		C(299)	-8.348	-3.801	4.230
C(260)	-3.243	-4.351	-2.530		C(300)	-8.713	-2.454	4.054
C(261)	-4.111	-5.623	-4.370		C(301)	1.460	5.902	1.465
C(262)	-4.346	-4.733	-3.309		C(302)	-0.819	5.556	1.632
N(263)	-1.788	-5.720	-3.826		C(303)	-2.035	5.723	2.470
C(264)	-2.821	-6.102	-4.597		C(304)	-0.865	5.037	0.336
N(265)	-1.154	-7.313	-5.830		C(305)	0.311	4.959	-0.407
C(266)	-0.742	-8.136	-6.805		N(306)	0.336	5.984	2.187
C(267)	-3.416	-7.615	-6.553		C(307)	1.500	5.399	0.166
C(268)	-2.471	-7.043	-5.698		C(308)	-3.281	5.185	2.148
C(269)	-1.623	-8.737	-7.699		C(309)	-4.181	6.252	4.103
C(270)	-2.984	-8.472	-7.564		C(310)	-4.387	5.438	2.975
C(271)	-6.100	-3.954	-1.693		N(311)	-1.861	6.453	3.580
C(272)	-7.383	-3.500	-1.409		C(312)	-2.902	6.739	4.378
C(273)	-6.641	-4.010	-4.041		N(313)	-1.248	7.817	5.747
C(274)	-5.703	-4.224	-3.015		C(314)	-0.854	8.567	6.785
C(275)	-7.921	-3.551	-3.753		C(315)	-3.528	8.129	6.411
C(276)	-8.326	-3.291	-2.431		C(316)	-2.567	7.590	5.554
C(277)	1.082	-1.941	5.397		C(317)	-1.753	9.137	7.683
C(278)	-1.213	-2.152	5.245		C(318)	-3.114	8.912	7.487
C(279)	-2.396	-3.009	5.522		C(319)	-6.120	4.633	1.344
C(280)	-1.321	-0.886	4.664		C(320)	-7.375	4.105	1.057

atom	x	y	z		atom	x	y	z
C(321)	-6.615	4.526	3.699		C(361)	-12.378	-1.247	2.158
C(322)	-5.716	4.862	2.671		C(362)	-10.605	3.246	-2.757
C(323)	-7.869	3.999	3.409		O(363)	-13.759	-1.995	-1.483
C(324)	-8.284	3.784	2.081		C(364)	-12.353	2.601	1.382
C(325)	0.349	2.073	-8.554		C(365)	-11.668	3.345	0.396
C(326)	-1.799	2.356	-7.732		C(366)	-12.312	3.725	-0.937
C(327)	-2.684	3.192	-6.876		C(367)	-11.770	2.872	-2.081
C(328)	-2.264	1.273	-8.481		C(368)	-12.313	-3.318	0.647
C(329)	-1.369	0.581	-9.296		C(369)	-10.623	-0.841	3.761
N(330)	-0.505	2.744	-7.774		C(370)	-10.023	2.426	-3.736
C(331)	-0.037	0.987	-9.339		C(371)	-12.397	-0.588	-3.665
C(332)	-4.012	2.890	-6.580		C(372)	-10.653	1.212	-4.045
C(333)	-4.159	4.972	-5.386		C(373)	-12.375	1.646	-2.419
C(334)	-4.772	3.775	-5.795		C(374)	-11.816	0.796	-3.391
N(335)	-2.112	4.310	-6.407		C(375)	-14.614	-2.765	-2.357
C(336)	-2.824	5.208	-5.710		C(376)	-14.788	-4.212	-1.900
N(337)	-0.737	6.380	-5.552		C(377)	-14.758	-0.907	2.225
C(338)	0.023	7.437	-5.239		C(378)	-15.422	-2.282	2.167
C(339)	-2.665	7.549	-4.742		C(379)	-14.753	1.630	-2.329
C(340)	-2.066	6.423	-5.309		C(380)	-15.879	1.125	-1.440
C(341)	-0.501	8.595	-4.669		C(381)	-14.519	3.588	1.530
C(342)	-1.870	8.648	-4.418		C(382)	-14.851	3.813	3.004
C(343)	-12.295	1.013	3.393		C(383)	-16.732	-2.354	2.971
C(344)	-11.783	-0.401	3.119		C(384)	-15.687	-5.039	-2.836
O(345)	-13.501	1.240	-1.735		C(385)	-15.863	2.820	3.591
O(346)	-13.515	-0.843	1.494		C(386)	-17.267	1.476	-1.989
C(347)	-12.405	-2.192	-1.655		C(387)	-6.512	2.104	-5.123
O(348)	-13.716	2.406	1.289		C(388)	-7.768	1.786	-4.622
C(349)	-10.007	-2.061	3.442		C(389)	-7.108	4.439	-5.125
C(350)	-10.604	-2.856	2.453		C(390)	-6.148	3.440	-5.366
C(351)	-11.775	-2.468	1.794		C(391)	-8.370	4.116	-4.636
C(352)	-11.687	-2.920	-0.686		C(392)	-8.722	2.785	-4.355
C(353)	-10.354	-3.247	-0.950		C(393)	-17.865	-1.475	2.427
C(354)	-9.708	-2.845	-2.127		C(394)	-17.159	-4.607	-2.850
C(355)	-10.412	-2.004	-3.002		C(395)	-16.161	3.078	5.071
C(356)	-11.741	-1.641	-2.772		C(396)	-18.402	0.982	-1.086
C(357)	-9.650	3.282	1.785		H(397)	2.385	-5.447	-2.057
C(358)	-10.311	2.399	2.652		H(398)	-1.669	-3.053	-0.730
C(359)	-11.647	2.035	2.463		H(399)	0.444	-2.554	0.458
C(360)	-10.337	3.697	0.635		H(400)	2.535	-3.790	-0.215

atom	x	y	z		atom	x	y	z
H(401)	-3.379	-3.644	-1.722		H(441)	-1.714	-0.256	-9.894
H(402)	-4.935	-5.950	-4.989		H(442)	0.690	0.486	-9.968
H(403)	0.326	-8.316	-6.860		H(443)	-4.460	1.977	-6.950
H(404)	-4.472	-7.407	-6.436		H(444)	-4.703	5.674	-4.768
H(405)	-1.247	-9.397	-8.472		H(445)	1.082	7.350	-5.456
H(406)	-3.706	-8.925	-8.235		H(446)	-3.733	7.581	-4.566
H(407)	-5.410	-4.126	-0.873		H(447)	0.152	9.428	-4.434
H(408)	-7.650	-3.296	-0.377		H(448)	-2.320	9.532	-3.979
H(409)	-6.365	-4.187	-5.076		H(449)	-13.374	1.071	3.278
H(410)	-8.627	-3.418	-4.568		H(450)	-12.060	1.270	4.432
H(411)	2.022	-2.384	5.706		H(451)	-10.132	-3.790	2.165
H(412)	-2.286	-0.474	4.397		H(452)	-9.824	-3.874	-0.240
H(413)	-0.232	0.842	3.987		H(453)	-9.904	-1.598	-3.872
H(414)	1.990	-0.130	4.673		H(454)	-9.775	1.989	3.503
H(415)	-3.872	-1.779	4.558		H(455)	-9.836	4.343	-0.079
H(416)	-5.261	-5.390	6.419		H(456)	-10.120	4.182	-2.493
H(417)	0.179	-7.590	7.955		H(457)	-13.392	3.609	-0.874
H(418)	-4.677	-6.974	7.708		H(458)	-12.105	4.779	-1.153
H(419)	-1.300	-9.315	8.986		H(459)	-13.393	-3.216	0.579
H(420)	-3.791	-8.985	8.853		H(460)	-12.083	-4.369	0.854
H(421)	-5.825	-1.033	5.177		H(461)	-10.189	-0.210	4.531
H(422)	-8.006	-0.423	4.293		H(462)	-13.473	-0.580	-3.503
H(423)	-6.834	-5.207	4.787		H(463)	-12.222	-0.842	-4.717
H(424)	-9.054	-4.588	3.982		H(464)	-10.231	0.577	-4.818
H(425)	2.368	6.257	1.939		H(465)	-15.567	-2.230	-2.350
H(426)	-1.803	4.718	-0.102		H(466)	-14.219	-2.741	-3.381
H(427)	0.290	4.573	-1.420		H(467)	-15.205	-4.222	-0.884
H(428)	2.440	5.364	-0.373		H(468)	-13.798	-4.684	-1.843
H(429)	-3.392	4.545	1.283		H(469)	-15.387	-0.142	1.763
H(430)	-5.013	6.495	4.751		H(470)	-14.592	-0.624	3.273
H(431)	0.216	8.715	6.892		H(471)	-15.616	-2.543	1.119
H(432)	-4.584	7.953	6.244		H(472)	-14.721	-3.029	2.561
H(433)	-1.390	9.739	8.508		H(473)	-14.790	2.725	-2.429
H(434)	-3.849	9.341	8.160		H(474)	-14.831	1.206	-3.341
H(435)	-5.459	4.891	0.522		H(475)	-15.749	1.551	-0.438
H(436)	-7.648	3.935	0.020		H(476)	-15.775	0.038	-1.335
H(437)	-6.328	4.662	4.737		H(477)	-15.435	3.436	0.949
H(438)	-8.546	3.774	4.227		H(478)	-14.002	4.465	1.126
H(439)	1.376	2.423	-8.556		H(479)	-13.921	3.802	3.590
H(440)	-3.307	0.981	-8.452		H(480)	-15.256	4.831	3.092

atom	x	y	z
H(481)	-17.067	-3.399	2.984
H(482)	-16.530	-2.088	4.019
H(483)	-15.628	-6.090	-2.525
H(484)	-15.281	-5.001	-3.857
H(485)	-15.492	1.796	3.465
H(486)	-16.795	2.880	3.012
H(487)	-17.384	1.043	-2.993
H(488)	-17.347	2.565	-2.113
H(489)	-5.788	1.308	-5.264
H(490)	-7.994	0.750	-4.388
H(491)	-6.878	5.479	-5.339
H(492)	-9.094	4.910	-4.476
H(493)	-18.789	-1.634	2.995
H(494)	-18.074	-1.709	1.376
H(495)	-17.624	-0.407	2.488
H(496)	-17.756	-5.277	-3.479
H(497)	-17.287	-3.591	-3.241
H(498)	-17.585	-4.630	-1.840
H(499)	-16.895	2.364	5.460
H(500)	-16.564	4.088	5.223
H(501)	-15.252	2.989	5.679
H(502)	-19.383	1.242	-1.500
H(503)	-18.332	1.428	-0.086
H(504)	-18.367	-0.108	-0.966
Zn(505)	0.141	-6.403	-4.391
Zn(506)	-0.143	-4.865	6.441
Zn(507)	-0.050	4.550	-6.442
Zn(508)	0.084	6.900	4.324

Table S2. Cartesian coordinates of mercaptopurine@Zn_4L_2 cages from B3LYP/6-31Gd optimization.

atom	x	y	z		atom	x	y	z
C(1)	-0.723	-8.455	-8.869		C(41)	-10.947	3.051	1.040
C(2)	-2.390	-7.464	-7.544		C(42)	-11.515	3.618	-0.268
C(3)	-2.672	-6.669	-6.318		C(43)	-10.921	3.014	-1.545
C(4)	-3.384	-7.944	-8.404		C(44)	-11.512	-3.579	0.031
C(5)	-3.021	-8.699	-9.525		C(45)	-9.968	-1.774	3.675
N(6)	-1.069	-7.727	-7.784		C(46)	-9.310	3.100	-3.404
C(7)	-1.669	-8.959	-9.765		C(47)	-11.404	-0.128	-3.755
C(8)	-3.937	-6.180	-5.955		C(48)	-9.797	1.853	-3.855
C(9)	-2.946	-5.288	-3.953		C(49)	-11.459	1.830	-2.102
C(10)	-4.096	-5.458	-4.750		C(50)	-10.861	1.201	-3.220
N(11)	-1.585	-6.450	-5.535		C(51)	-13.799	-2.393	-2.940
C(12)	-1.717	-5.801	-4.355		C(52)	-14.133	-3.864	-2.720
N(13)	0.661	-6.103	-4.126		C(53)	-13.974	-1.543	1.164
C(14)	1.804	-6.077	-3.404		C(54)	-14.388	-2.372	2.378
C(15)	-0.513	-5.242	-2.207		C(55)	-13.894	1.782	-2.119
C(16)	-0.492	-5.693	-3.535		C(56)	-15.033	1.112	-1.372
C(17)	1.856	-5.645	-2.078		C(57)	-13.946	2.985	1.997
C(18)	0.673	-5.213	-1.473		C(58)	-14.432	2.819	3.433
C(19)	-11.621	0.170	3.527		C(59)	-15.060	-4.433	-3.821
C(20)	-11.018	-1.139	3.005		C(60)	-15.399	1.640	3.667
O(21)	-12.604	1.279	-1.545		C(61)	-16.425	1.614	-1.820
O(22)	-12.552	-1.068	1.190		C(62)	-6.307	-4.288	-5.162
C(23)	-11.529	-2.063	-2.052		C(63)	-7.445	-3.647	-4.669
O(24)	-13.016	1.874	1.580		C(64)	-5.644	-4.813	-2.900
C(25)	-9.425	-2.997	3.222		C(65)	-5.370	-4.871	-4.285
C(26)	-9.962	-3.559	2.045		C(66)	-7.708	-3.567	-3.282
C(27)	-11.006	-2.954	1.335		C(67)	-6.781	-4.183	-2.412
C(28)	-10.862	-2.999	-1.225		C(68)	0.002	-9.009	4.398
C(29)	-9.584	-3.426	-1.612		C(69)	-2.122	-8.094	4.761
C(30)	-8.939	-2.921	-2.762		C(70)	-2.878	-6.980	5.383
C(31)	-9.547	-1.832	-3.424		C(71)	-2.730	-9.187	4.135
C(32)	-10.818	-1.366	-3.065		C(72)	-1.930	-10.220	3.635
C(33)	-9.165	3.027	2.729		N(73)	-0.765	-8.013	4.890
C(34)	-9.810	1.937	3.350		C(74)	-0.540	-10.131	3.766
C(35)	-11.025	1.419	2.880		C(75)	-4.181	-6.601	5.052
C(36)	-9.709	3.501	1.517		C(76)	-4.030	-4.855	6.715
C(37)	-11.549	-1.749	1.842		C(77)	-4.769	-5.472	5.673
C(38)	-9.864	3.639	-2.221		N(78)	-2.161	-6.287	6.295
O(39)	-12.889	-1.858	-1.869		C(79)	-2.729	-5.277	6.991
C(40)	-11.667	2.103	1.818		N(80)	-0.494	-4.905	7.788

atom	x	y	z		atom	x	y	z
C(81)	0.404	-4.418	8.672		C(121)	-1.577	11.442	-4.859
C(82)	-2.270	-3.941	9.101		C(122)	-4.584	7.231	-5.660
C(83)	-1.822	-4.667	7.993		C(123)	-4.030	5.228	-6.880
C(84)	0.025	-3.687	9.800		C(124)	-4.945	5.916	-6.046
C(85)	-1.336	-3.449	10.019		N(125)	-2.401	6.956	-6.607
C(86)	-7.016	-5.658	4.519		C(126)	-2.768	5.764	-7.126
C(87)	-8.126	-5.059	3.926		C(127)	0.587	4.997	-8.341
C(88)	-6.233	-3.490	5.234		C(128)	-1.968	4.175	-8.931
C(89)	-6.029	-4.886	5.171		C(129)	-1.706	5.104	-7.917
C(90)	-8.305	-3.655	3.937		C(130)	0.400	4.072	-9.371
C(91)	-7.337	-2.895	4.632		C(131)	-0.901	3.659	-9.673
C(92)	-0.510	4.912	9.841		C(132)	-7.198	5.926	-4.870
C(93)	-2.408	5.113	8.481		C(133)	-8.228	5.246	-4.219
C(94)	-2.902	5.438	7.120		C(134)	-6.212	3.820	-5.497
C(95)	-3.246	4.821	9.561		C(135)	-6.143	5.232	-5.503
C(96)	-2.681	4.572	10.818		C(136)	-8.264	3.832	-4.166
C(97)	-1.290	4.614	10.961		C(137)	-7.243	3.141	-4.856
C(98)	-4.155	5.085	6.609		C(138)	-16.466	-3.808	-3.854
C(99)	-3.550	6.161	4.536		C(139)	-16.779	1.825	3.013
C(100)	-4.487	5.395	5.268		C(140)	-16.805	1.242	-3.264
N(101)	-1.992	6.070	6.346		C(141)	-15.897	-2.717	2.366
C(102)	-2.312	6.473	5.098		C(142)	-16.328	-3.662	1.232
N(103)	0.012	7.046	4.937		N(143)	-0.439	5.514	-7.632
C(104)	1.052	7.717	4.400		N(144)	-1.051	5.161	8.629
C(105)	-1.456	8.085	3.334		H(145)	0.336	-8.636	-9.012
C(106)	-1.232	7.219	4.411		H(146)	-4.431	-7.753	-8.204
C(107)	0.901	8.600	3.328		H(147)	-3.783	-9.082	-10.194
C(108)	-0.376	8.787	2.790		H(148)	-1.352	-9.542	-10.621
C(109)	-6.831	4.451	5.378		H(149)	-4.799	-6.367	-6.582
C(110)	-7.939	3.868	4.765		H(150)	-3.024	-4.711	-3.044
C(111)	-5.770	4.694	3.222		H(151)	2.698	-6.413	-3.910
C(112)	-5.711	4.866	4.624		H(152)	-1.440	-4.933	-1.744
C(113)	-7.990	3.675	3.365		H(153)	2.791	-5.630	-1.531
C(114)	-6.883	4.119	2.612		H(154)	0.676	-4.867	-0.446
C(115)	-0.829	10.305	-5.178		H(155)	-12.695	0.164	3.349
C(116)	-2.771	9.041	-5.537		H(156)	-11.459	0.217	4.610
C(117)	-3.307	7.721	-5.957		H(157)	-9.545	-4.486	1.661
C(118)	-3.576	10.140	-5.227		H(158)	-9.129	-4.239	-1.055
C(119)	-2.972	11.357	-4.887		H(159)	-9.023	-1.345	-4.242
N(120)	-1.406	9.130	-5.514		H(160)	-9.393	1.511	4.261

atom	x	y	z		atom	x	y	z
H(161)	-9.208	4.307	0.988		H(201)	-4.711	-7.112	4.258
H(162)	-9.487	4.583	-1.835		H(202)	-4.465	-4.031	7.265
H(163)	-12.593	3.460	-0.279		H(203)	1.445	-4.638	8.470
H(164)	-11.343	4.701	-0.286		H(204)	-3.330	-3.796	9.271
H(165)	-12.592	-3.462	-0.049		H(205)	0.775	-3.332	10.496
H(166)	-11.308	-4.655	0.068		H(206)	-1.666	-2.909	10.898
H(167)	-9.610	-1.345	4.607		H(207)	-6.940	-6.741	4.506
H(168)	-12.487	-0.136	-3.642		H(208)	-8.882	-5.689	3.471
H(169)	-11.187	-0.182	-4.828		H(209)	-5.487	-2.849	5.693
H(170)	-9.396	1.423	-4.768		H(210)	-7.430	-1.815	4.661
H(171)	-14.679	-1.755	-2.866		H(211)	0.570	4.966	9.907
H(172)	-13.324	-2.240	-3.916		H(212)	-4.322	4.825	9.441
H(173)	-14.616	-3.983	-1.741		H(213)	-3.316	4.365	11.671
H(174)	-13.201	-4.445	-2.697		H(214)	-0.820	4.434	11.920
H(175)	-14.115	-2.074	0.224		H(215)	-4.840	4.509	7.217
H(176)	-14.528	-0.604	1.121		H(216)	-3.779	6.476	3.528
H(177)	-13.809	-3.305	2.421		H(217)	2.020	7.547	4.853
H(178)	-14.159	-1.814	3.296		H(218)	-2.457	8.241	2.952
H(179)	-13.924	2.873	-2.002		H(219)	1.758	9.137	2.940
H(180)	-13.905	1.554	-3.191		H(220)	-0.534	9.484	1.975
H(181)	-14.888	1.298	-0.303		H(221)	-6.864	4.623	6.449
H(182)	-14.957	0.028	-1.512		H(222)	-8.798	3.598	5.370
H(183)	-14.764	2.924	1.279		H(223)	-4.928	4.957	2.592
H(184)	-13.423	3.939	1.867		H(224)	-6.873	3.973	1.538
H(185)	-13.560	2.735	4.096		H(225)	0.253	10.327	-5.179
H(186)	-14.938	3.755	3.713		H(226)	-4.655	10.067	-5.287
H(187)	-15.153	-5.513	-3.658		H(227)	-3.582	12.226	-4.665
H(188)	-14.577	-4.314	-4.802		H(228)	-1.077	12.369	-4.609
H(189)	-14.937	0.712	3.303		H(229)	-5.259	7.826	-5.060
H(190)	-15.533	1.515	4.749		H(230)	-4.288	4.261	-7.289
H(191)	-16.481	2.705	-1.694		H(231)	1.577	5.350	-8.083
H(192)	-17.173	1.193	-1.136		H(232)	-2.987	3.896	-9.171
H(193)	-6.137	-4.309	-6.234		H(233)	1.250	3.705	-9.934
H(194)	-8.156	-3.224	-5.371		H(234)	-1.087	2.966	-10.486
H(195)	-4.971	-5.296	-2.197		H(235)	-7.241	7.010	-4.903
H(196)	-6.946	-4.144	-1.342		H(236)	-9.035	5.817	-3.774
H(197)	1.072	-8.902	4.530		H(237)	-5.424	3.230	-5.952
H(198)	-3.810	-9.255	4.075		H(238)	-7.231	2.056	-4.850
H(199)	-2.386	-11.087	3.172		H(239)	-17.094	-4.309	-4.597
H(200)	0.108	-10.919	3.404		H(240)	-16.443	-2.743	-4.117

atom	x	y	z		atom	x	y	z
H(241)	-16.964	-3.906	-2.882		C(281)	0.080	1.124	4.635
H(242)	-17.435	0.979	3.241		N(282)	-0.096	3.654	5.802
H(243)	-16.715	1.904	1.921		C(283)	-1.171	1.697	4.883
H(244)	-17.272	2.731	3.384		C(284)	3.603	3.561	5.618
H(245)	-17.827	1.564	-3.490		C(285)	4.373	5.574	6.700
H(246)	-16.762	0.156	-3.417		C(286)	4.679	4.400	5.977
H(247)	-16.147	1.715	-4.003		N(287)	2.029	5.056	6.620
H(248)	-16.144	-3.180	3.329		C(288)	3.041	5.869	7.019
H(249)	-16.482	-1.787	2.317		N(289)	1.255	7.249	7.876
H(250)	-16.205	-3.205	0.242		C(290)	0.771	8.305	8.568
H(251)	-17.383	-3.933	1.335		C(291)	3.493	7.940	8.428
H(252)	-15.746	-4.593	1.252		C(292)	2.607	7.060	7.796
C(253)	-1.950	6.261	-3.317		C(293)	1.603	9.220	9.216
C(254)	0.301	5.675	-3.482		C(294)	2.987	9.031	9.145
C(255)	1.565	5.842	-4.234		C(295)	6.411	2.670	5.501
C(256)	0.222	4.962	-2.277		C(296)	7.595	2.265	4.897
C(257)	-0.989	4.906	-1.586		C(297)	6.942	4.973	5.001
N(258)	-0.786	6.303	-4.004		C(298)	6.037	4.030	5.530
C(259)	-2.096	5.583	-2.107		C(299)	8.120	4.560	4.375
C(260)	2.761	5.241	-3.857		C(300)	8.455	3.191	4.265
C(261)	3.866	6.387	-5.661		C(301)	-1.489	-4.078	3.993
C(262)	3.954	5.496	-4.565		C(302)	0.809	-4.366	3.704
N(263)	1.505	6.658	-5.310		C(303)	2.049	-4.970	4.238
C(264)	2.631	6.956	-6.006		C(304)	0.805	-3.505	2.596
N(265)	1.123	8.285	-7.348		C(305)	-0.398	-2.909	2.209
C(266)	0.843	9.168	-8.333		N(306)	-0.333	-4.662	4.381
C(267)	3.463	8.465	-7.881		C(307)	-1.568	-3.183	2.924
C(268)	2.423	7.924	-7.117		C(308)	3.314	-4.650	3.752
C(269)	1.837	9.740	-9.131		C(309)	4.280	-6.049	5.461
C(270)	3.169	9.382	-8.898		C(310)	4.468	-5.175	4.369
C(271)	5.402	4.550	-2.757		N(311)	1.895	-5.818	5.283
C(272)	6.554	3.912	-2.305		C(312)	2.981	-6.367	5.885
C(273)	6.226	4.466	-5.025		N(313)	1.331	-7.443	7.283
C(274)	5.207	4.846	-4.126		C(314)	0.948	-8.284	8.270
C(275)	7.377	3.818	-4.574		C(315)	3.627	-8.026	7.706
C(276)	7.577	3.530	-3.203		C(316)	2.661	-7.306	6.994
C(277)	-1.209	2.964	5.468		C(317)	1.864	-9.029	9.016
C(278)	1.122	3.097	5.555		C(318)	3.226	-8.895	8.727
C(279)	2.296	3.912	5.944		C(319)	5.984	-4.568	2.476
C(280)	1.241	1.825	4.972		C(320)	7.175	-4.044	1.979

atom	x	y	z		atom	x	y	z
C(321)	6.855	-4.407	4.729		C(361)	11.620	1.680	1.783
C(322)	5.792	-4.745	3.864		C(362)	10.140	-3.442	-2.503
C(323)	8.040	-3.864	4.227		O(363)	12.861	2.132	-1.860
C(324)	8.228	-3.654	2.838		C(364)	12.024	-2.147	1.528
C(325)	-0.682	-4.293	-8.222		C(365)	11.317	-3.045	0.687
C(326)	1.618	-4.414	-7.836		C(366)	11.894	-3.520	-0.652
C(327)	2.700	-5.150	-7.145		C(367)	11.243	-2.859	-1.870
C(328)	1.852	-3.349	-8.714		C(368)	11.347	3.608	0.132
C(329)	0.768	-2.754	-9.366		C(369)	10.285	1.526	3.789
N(330)	0.361	-4.885	-7.603		C(370)	9.501	-2.829	-3.603
C(331)	-0.523	-3.228	-9.112		C(371)	11.538	0.437	-3.882
C(332)	3.961	-4.628	-6.865		C(372)	9.961	-1.560	-4.014
C(333)	4.558	-6.741	-5.878		C(373)	11.745	-1.640	-2.390
C(334)	4.907	-5.392	-6.138		C(374)	11.067	-0.945	-3.418
N(335)	2.358	-6.399	-6.759		C(375)	13.742	2.774	-2.889
C(336)	3.282	-7.215	-6.205		C(376)	14.080	4.212	-2.508
N(337)	1.414	-8.711	-5.942		C(377)	14.012	1.267	1.063
C(338)	0.864	-9.928	-5.739		C(378)	14.465	2.384	2.000
C(339)	3.605	-9.691	-5.726		C(379)	14.178	-1.610	-2.538
C(340)	2.776	-8.585	-5.933		C(380)	15.366	-0.954	-1.858
C(341)	1.637	-11.073	-5.526		C(381)	14.331	-2.992	1.601
C(342)	3.029	-10.951	-5.523		C(382)	14.774	-3.028	3.060
C(343)	11.976	-0.323	3.343		C(383)	16.004	2.421	2.164
C(344)	11.288	0.992	2.972		C(384)	15.011	4.900	-3.534
O(345)	12.925	-1.116	-1.881		C(385)	15.705	-1.879	3.487
O(346)	12.525	1.155	0.886		C(386)	16.709	-1.444	-2.438
C(347)	11.492	2.242	-2.043		C(387)	6.270	-3.359	-5.553
O(348)	13.370	-1.874	1.305		C(388)	7.354	-2.742	-4.930
C(349)	9.598	2.710	3.453		C(389)	7.181	-5.519	-5.008
C(350)	9.960	3.374	2.262		C(390)	6.135	-4.766	-5.594
C(351)	10.958	2.876	1.418		C(391)	8.264	-4.904	-4.382
C(352)	10.738	3.040	-1.149		C(392)	8.379	-3.492	-4.303
C(353)	9.423	3.372	-1.508		C(393)	16.774	2.801	0.888
C(354)	8.843	2.931	-2.718		C(394)	16.424	4.298	-3.615
C(355)	9.555	1.976	-3.472		C(395)	16.160	-2.000	4.950
C(356)	10.852	1.581	-3.126		C(396)	17.919	-0.777	-1.764
C(357)	9.478	-3.054	2.313		H(397)	-2.785	6.785	-3.756
C(358)	10.125	-2.018	3.013		H(398)	1.093	4.462	-1.873
C(359)	11.371	-1.523	2.617		H(399)	-1.089	4.334	-0.671
C(360)	10.060	-3.497	1.108		H(400)	-3.048	5.562	-1.589

atom	x	y	z		atom	x	y	z
H(401)	2.784	4.550	-3.027		H(441)	0.932	-1.950	-10.074
H(402)	4.762	6.646	-6.209		H(442)	-1.386	-2.800	-9.607
H(403)	-0.201	9.418	-8.475		H(443)	4.194	-3.619	-7.173
H(404)	4.493	8.194	-7.689		H(444)	5.252	-7.394	-5.365
H(405)	1.573	10.446	-9.909		H(445)	-0.218	-9.978	-5.760
H(406)	3.967	9.811	-9.493		H(446)	4.683	-9.587	-5.760
H(407)	4.662	4.861	-2.026		H(447)	1.158	-12.033	-5.380
H(408)	6.656	3.688	-1.248		H(448)	3.659	-11.822	-5.381
H(409)	6.116	4.663	-6.087		H(449)	13.040	-0.272	3.117
H(410)	8.154	3.566	-5.287		H(450)	11.882	-0.468	4.425
H(411)	-2.155	3.444	5.680		H(451)	9.440	4.284	1.979
H(412)	2.209	1.377	4.776		H(452)	8.890	4.088	-0.890
H(413)	0.156	0.140	4.185		H(453)	9.088	1.533	-4.348
H(414)	-2.092	1.181	4.628		H(454)	9.652	-1.585	3.890
H(415)	3.797	2.681	5.023		H(455)	9.558	-4.259	0.519
H(416)	5.174	6.230	7.013		H(456)	9.774	-4.396	-2.132
H(417)	-0.307	8.408	8.601		H(457)	12.962	-3.314	-0.670
H(418)	4.562	7.780	8.383		H(458)	11.766	-4.606	-0.734
H(419)	1.178	10.053	9.763		H(459)	12.432	3.591	0.027
H(420)	3.663	9.716	9.643		H(460)	11.040	4.656	0.231
H(421)	5.760	1.923	5.944		H(461)	10.057	1.025	4.726
H(422)	7.838	1.209	4.865		H(462)	12.616	0.505	-3.748
H(423)	6.702	6.032	5.026		H(463)	11.329	0.536	-4.954
H(424)	8.787	5.307	3.959		H(464)	9.495	-1.070	-4.863
H(425)	-2.371	-4.329	4.563		H(465)	14.627	2.138	-2.912
H(426)	1.710	-3.285	2.039		H(466)	13.244	2.733	-3.865
H(427)	-0.420	-2.231	1.363		H(467)	14.559	4.215	-1.520
H(428)	-2.512	-2.710	2.661		H(468)	13.148	4.786	-2.420
H(429)	3.427	-3.959	2.929		H(469)	14.350	1.424	0.041
H(430)	5.142	-6.484	5.950		H(470)	14.354	0.289	1.406
H(431)	-0.117	-8.355	8.458		H(471)	14.122	3.358	1.625
H(432)	4.680	-7.925	7.474		H(472)	14.010	2.249	2.991
H(433)	1.519	-9.693	9.798		H(473)	14.213	-2.703	-2.445
H(434)	3.965	-9.459	9.285		H(474)	14.129	-1.359	-3.606
H(435)	5.203	-4.839	1.774		H(475)	15.316	-1.163	-0.783
H(436)	7.290	-3.911	0.909		H(476)	15.285	0.134	-1.969
H(437)	6.749	-4.541	5.801		H(477)	15.172	-2.792	0.933
H(438)	8.844	-3.620	4.912		H(478)	13.858	-3.937	1.312
H(439)	-1.663	-4.696	-8.006		H(479)	13.889	-3.066	3.712
H(440)	2.862	-3.019	-8.922		H(480)	15.301	-3.983	3.209

atom	x	y	z		atom	x	y	z
H(481)	16.242	3.145	2.953		H(521)	-6.664	4.762	-1.238
H(482)	16.354	1.446	2.531		N(522)	-4.731	4.135	-0.560
H(483)	15.089	5.960	-3.260		S(523)	-8.302	-0.240	0.036
H(484)	14.540	4.879	-4.528		C(524)	-6.282	-0.344	1.967
H(485)	15.198	-0.916	3.337		C(525)	-6.743	-0.828	0.739
H(486)	16.586	-1.871	2.829		N(526)	-5.954	-1.704	0.082
H(487)	16.739	-1.247	-3.519		C(527)	-4.772	-2.095	0.641
H(488)	16.782	-2.535	-2.323		N(528)	-4.257	-1.669	1.801
H(489)	5.504	-2.719	-5.974		C(529)	-5.023	-0.768	2.461
H(490)	7.399	-1.658	-4.913		N(530)	-6.765	0.548	2.903
H(491)	7.176	-6.602	-5.065		H(531)	-8.416	-1.239	-0.911
H(492)	9.060	-5.523	-3.984		H(532)	-4.194	-2.805	0.066
H(493)	17.845	2.892	1.096		H(533)	-7.658	1.031	2.873
H(494)	16.432	3.767	0.495		C(534)	-5.807	0.643	3.890
H(495)	16.659	2.051	0.095		H(535)	-5.932	1.295	4.739
H(496)	17.055	4.882	-4.292		N(536)	-4.742	-0.131	3.666
H(497)	16.419	3.267	-3.989		S(537)	5.291	0.288	-2.903
H(498)	16.909	4.298	-2.631		C(538)	4.762	-2.081	-1.491
H(499)	16.827	-1.177	5.226		C(539)	4.494	-0.714	-1.612
H(500)	16.705	-2.937	5.118		N(540)	3.618	-0.160	-0.759
H(501)	15.305	-1.983	5.637		C(541)	3.015	-0.942	0.179
H(502)	18.858	-1.147	-2.187		N(542)	3.183	-2.267	0.351
H(503)	17.936	-0.982	-0.686		C(543)	4.074	-2.829	-0.500
H(504)	17.899	0.311	-1.899		N(544)	5.601	-2.984	-2.118
Zn(505)	-0.356	7.291	-6.117		H(545)	5.065	1.502	-2.297
Zn(506)	0.063	5.765	6.827		H(546)	2.338	-0.434	0.852
Zn(507)	0.321	-6.857	-6.372		H(547)	6.255	-2.801	-2.872
Zn(508)	-0.039	-6.260	6.067		C(548)	5.399	-4.204	-1.511
S(509)	-5.470	-0.407	-2.820		H(549)	5.942	-5.085	-1.812
C(510)	-4.947	2.019	-1.458		N(550)	4.483	-4.160	-0.541
C(511)	-4.489	0.737	-1.764		S(551)	7.964	0.311	0.372
N(512)	-3.287	0.366	-1.291		C(552)	5.858	0.385	2.219
C(513)	-2.553	1.258	-0.567		C(553)	6.503	1.039	1.162
N(514)	-2.889	2.527	-0.271		N(554)	5.998	2.215	0.748
C(515)	-4.106	2.899	-0.721		C(555)	4.893	2.722	1.366
N(516)	-6.096	2.742	-1.712		N(556)	4.206	2.164	2.374
H(517)	-5.756	-1.289	-1.752		C(557)	4.710	0.982	2.792
H(518)	-1.596	0.904	-0.207		N(558)	6.061	-0.782	2.938
H(519)	-6.928	2.412	-2.185		H(559)	8.319	1.434	-0.348
C(520)	-5.914	3.992	-1.163		H(560)	4.545	3.678	0.998

atom	x	y	z
H(561)	6.794	-1.468	2.803
C(562)	5.064	-0.844	3.890
H(563)	5.000	-1.660	4.590
N(564)	4.228	0.193	3.838
H(565)	4.146	-4.954	0.059
H(566)	3.393	0.376	4.448
H(561)	6.794	-1.468	2.803
C(562)	5.064	-0.844	3.890
H(563)	5.000	-1.660	4.590
N(564)	4.228	0.193	3.838
H(565)	4.146	-4.954	0.059
H(566)	3.393	0.376	4.448

Table S3 Energies of $\mathbf{Zn_4L1_2}$ cage, mercaptopurine, and mercaptopurine@$\mathbf{Zn_4L1_2}$ cage obtained from computational study (B3LYP/6-31Gd).

System	E (cage) (au)	E (mercaptopurine) (au)	E (mercaptopurine@cage) (au)	E_s [#] (kcal/mol)
mercaptopurine@cage complex	-18917.3776588	-810.1467574	-22157.8924983	-45.3

[#]E_s denotes the complex stabilization energy.

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