Electronic Supplementary Information (ESI†)

$[Cd(H_2O)_6]@\{Cd_6Cl_4(nico)_{12}[Hg(Tab)_2(\mu\text{-}Cl)]_2\}$: a heterometallic host-guest icosidodecahedron cage *via* hierarchical assembly

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Experimental Section

Materials and methods. $[Hg(Tab)_2](PF_6)_2$ was prepared according to the literature method.[S1] Other chemicals and reagents were obtained from commercial sources and used as received. All solvents were pre-dried over activated molecular sieves and refluxed over appropriate drying agents under argon. IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm^{-1}). Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer.

Preparation of $[Hg(Tab)_2(nico)]_2(PF_6)_2$ (2). Et_3N was added to a solution of nicotinic acid (0.25 g, 2 mmol) in H_2O (4 mL) until its pH reaches 7.0. The resulting colourless solution was transferred to a solution containing **1** (0.83 g, 1 mmol) in MeCN/MeOH (15 mL, 3:2, *v*/*v*) and the colourless mixture briefly stirred for 0.5 h to form a homogeneous solution. Upon filtration, diethyl ether (40 mL) was carefully layered onto the filtrate at ambient temperature for two weeks to give colorless long needle crystals of **2**·3MeCN·2MeOH. These crystals were collected by filtration, washed by Et_2O and dried *in vacuo*. Yield: 0.63 g (78% based on Hg). Anal. Calcd. for **2**·3MeCN·$2H_2O$ ($C_{54}H_{73}N_9F_{12}P_2S_4Hg_2O_6$): C 36.77, H 4.17, N 7.15%; found: C 36.12, H 4.34, N 7.51%. IR (KBr, cm^{-1}): 3405 (br), 1615 (s), 1568 (w), 1491 (s), 1375 (s), 1321 (w), 1190 (w), 1127 (m), 1011 (w), 958 (w), 839 (s), 761 (w), 746 (w), 670 (w), 558 (s) cm^{-1}.

Preparation of $[Cd(H_2O)_6]$@$\{Cd_6Cl_4(nico)_{12}[Hg(Tab)_2(\mu\text{-}Cl)]_2\}$ (3). A solution of $CdCl_2·2.5H_2O$ (0.23 g, 1 mmol) in MeOH (3 mL) and H_2O (1 mL) was added to a solution of **2** (0.92 g, 1 mmol) in DMF (1 mL) and CH_3OH (6 mL) while stirring. The colourless mixture was stirred for 0.5 h to give a homogeneous solution. Upon filtration, diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for two weeks to give forming colourless blocks of **3**·10DMF·$3H_2O$. These crystals were collected by filtration, washed by Et_2O and dried *in vacuo*. Yield: 0.29 g (45% based on $CdCl_2$). Anal. Calcd. for **3**·10DMF·$3H_2O$ ($C_{138}H_{188}N_{26}Hg_2Cd_7Cl_6O_{43}S_4$): C 37.43, H 4.28, N 8.22%; found: C 37.04, H 4.52, N 8.48%. IR (KBr, cm^{-1}): 3441(br), 1616 (s), 1566 (m), 1487(m), 1406 (s), 1199 (w), 1124 (w), 1093 (w), 1031 (w), 949 (w), 848 (w), 756 (m), 704(w), 621 (w), 552 (w) cm^{-1}.

Preparation of $[Hg(Tab)_2][CdCl_4]$ (4). A solution of $CdCl_2·2.5H_2O$ (0.68 g, 3 mmol) in MeOH (3 mL) and H_2O (1 mL) was added to a solution of **2** (0.92 g, 1 mmol) in DMF (1 mL) and CH_3OH (6 mL) while stirring. The

colourless mixture was stirred for 0.5 h to give a homogeneous solution. Upon filtration, diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for two weeks to give forming colourless blocks of **4**·MeOH. The colourless prism crystals were collected by filtration, washed by Et_2O and dried *in vacuo*. Yield: 0.70 g (85% based on Hg). Anal. Calcd. for **4**·MeOH ($C_{19}H_{30}CdCl_4HgN_2OS_2$): C 27.78, H 3.69, N 3.41%; found: C 27.53, H 3.47, N 3.17%. IR (KBr, cm^{-1}): 3420 (br), 3085 (w), 3024 (w), 2963 (w), 1585 (w), 1488 (s), 1409 (m), 1262(w), 1127 (m), 1085 (m), 1015 (m), 959 (w), 806 (m), 746 (w), 551 (m) cm^{-1}.

Single crystal X-ray structure determinations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite-monochromated Mo Kα (λ = 0.71073 Å). Single crystals of **2**·3MeCN·2MeOH, **3**·10DMF·$3H_2O$ and **4**·MeOH suitable for single crystal X-ray analysis were obtained directly from the above preparations. These crystals were mounted on glass fibers and cooled at 193 K for data collection. The collected data were reduced by using the program CrystalClear (Rigaku and MSc, Ver. 1.3, 2001), and an absorption correction (multi-scan) was applied.[S2]

The crystal structures of **2**·3MeCN·2MeOH, **3**·10DMF·$3H_2O$ and **4**·MeOH were solved by direct methods and refined on F^2 by full-matrixleast-squares using anisotropic displacement parameters for all non-hydrogen atoms.[S3] All hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups; C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ for phenyl groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups. Some important Relevant collection and refinement parameters for **2**·3MeCN·2MeOH, **3**·10DMF·$3H_2O$ and **4**·MeOH are summarized in Table S1. CCDC number of 1558989 for **2**·3MeCN·2MeOH, 1558990 for **3**·10DMF·$3H_2O$, 1558991 for **4**·MeOH contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Summary of crystallographic data and structure refinement parameters for **2**·3MeCN·2MeOH, **3**·10DMF·$2H_2O$ and **4**·MeOH

Compound	**2**·3MeCN·2MeOH	**3**·10DMF·$3H_2O$	**4**·MeOH
Molecular Formula	$C_{56}H_{77}F_{12}Hg_2N_9O_6P_2S_4$	$C_{138}H_{188}Cd_7Cl_6Hg_2N_{26}O_{43}S_4$	$C_{19}H_{30}CdCl_4HgN_2OS_2$
Formula weight	1791.63	4428.14	821.37

Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Size	0.50 × 0.21 × 0.12	0.30 × 0.18× 0.12	0.40×0.14×0.12
a (Å)	8.4455(17)	16.080(2)	12.542(3)
b (Å)	10.670(2)	16.7412(13)	8.8863(18)
c (Å)	19.8160(15)	20.135(3)	24.244(5)
α(°)	93.09(2)	101.243(2)	90
β(°)	99.53(3)	108.605(3)	93.86(3)
γ(°)	94.56(2)	111.309(2)	90
V (Å^3)	1751.4(5)	4479.3(10)	2695.9(10)
Z	1	1	4
T/K	193(2)	193(2)	193(2)
D_{calc} (g cm^{-3})	1.699	1.642	2.024
λ(Mo-Kα) (Å)	0.71073	0.71073	0.71073
μ(cm^{-1})	46.27	27.33	70.43
$2\lambda_{max}$ (°)	50.7	50.7	50.7
Total reflections	17096	43855	24838
Unique reflections	6363(R_{int} = 0.0314)	16267 (R_{int} = 0.0469)	4752(R_{int} = 0.0601)
No. observations	5323 ($I > 2.00\ \sigma(I)$)	12200($I > 2.00\ \sigma(I)$)	4249 ($I > 2.00\sigma(I)$)
No. parameters	430	1043	275
R[a]	0.0338	0.0513	0.0427
wR[b]	0.0711	0.1161	0.0811
GOF[c]	1.034	1.020	1.193

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o||$. [b] $wR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma[w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

Table S2 Selected bond distances (Å) and angles (º) for **2**–**4**

Compound **2**			
Hg(1)-S(1)	2.3702(13)	Hg(1)-S(2)	2.3621(13)

Hg(1)-N(3)	2.480(4)	S(1)-Hg(1)-S(2)	166.69(4)
S(1)-Hg(1)-N(3)	103.66(10)	S(2)-Hg(1)-N(3)	89.28(10)

Compound **3**

Hg(1)-S(1)	2.337(2)	Hg(1)-S(2)	2.3399(19)
Hg(1)-Cl(1)	2.9113(15)	Cd(1)-N(4)	2.298(5)
Cd(1)-N(8)#1	2.319(6)	Cd(1)-O(7)	2.422(4)
Cd(1)-O(1)	2.424(4)	Cd(1)-O(8)	2.507(4)
Cd(1)-O(2)	2.530(4)	Cd(1)-Cl(1)	2.5905(15)
Cd(2)-N(6)#1	2.339(5)	Cd(2)-N(3)	2.340(5)
Cd(2)-O(6)	2.419(5)	Cd(2)-O(9)#1	2.451(5)
Cd(2)-O(10)#1	2.488(4)	Cd(2)-Cl(2)	2.5509(16)
Cd(2)-O(5)	2.566(4)	Cd(3)-N(7)	2.320(5)
Cd(3)-N(5)	2.343(5)	Cd(3)-O(4)	2.406(4)
Cd(3)-O(3)	2.523(5)	Cd(3)-O(11)	2.545(4)
Cd(3)-O(12)	2.428(4)	Cd(3)-Cl(3)	2.5160(15)
Cd(4)-O(2W)	2.224(4)	Cd(4)-O(2W)#2	2.224(4)
Cd(4)-O(1W)#2	2.200(4)	Cd(4)-O(1W)	2.200(4)
Cd(4)-O(3W)	2.283(4)	Cd(4)-O(3W)#2	2.283(4)
S(1)-Hg(1)-S(2)	173.37(6)	S(1)-Hg(1)-Cl(1)	84.83(6)
S(2)-Hg(1)-Cl(1)	101.64(5)	O(8)-Cd(1)-O(2)	81.37(14)
O(7)-Cd(1)-O(8)	53.59(13)	O(1)-Cd(1)-O(8)	132.93(14)
N(4)-Cd(1)-O(2)	88.72(17)	N(8)#1-Cd(1)-O(2)	81.53(18)
O(7)-Cd(1)-O(2)	134.98(14)	O(1)-Cd(1)-O(2)	52.26(14)
N(4)-Cd(1)-O(1)	86.05(18)	N(8)#1-Cd(1)-O(1)	95.50(17)
N(4)-Cd(1)-N(8)#1	166.2(2)	N(8)#1-Cd(1)-O(7)	91.97(18)

N(4)-Cd(1)-O(7)	88.05(18)	N(4)-Cd(1)-O(8)	85.15(17)
N(4)-Cd(1)-Cl(1)	100.03(14)	N(8)#1-Cd(1)-Cl(1)	93.72(16)
O(7)-Cd(1)-Cl(1)	89.86(11)	O(1)-Cd(1)-Cl(1)	83.97(11)
O(8)-Cd(1)-Cl(1)	143.10(10)	O(2)-Cd(1)-Cl(1)	134.82(11)
O(7)-Cd(1)-O(1)	170.59(15)	N(8)#1-Cd(1)-O(8)	83.81(17)
O(6)-Cd(2)-Cl(2)	87.69(11)	O(6)-Cd(2)-O(5)	52.95(14)
N(6)#1-Cd(2)-Cl(2)	99.27(14)	N(3)-Cd(2)-Cl(2)	96.82(13)
N(6)#1-Cd(2)-O(9)#1	85.77(19)	N(3)-Cd(2)-O(9)#1	85.47(17)
N(6)#1-Cd(2)-N(3)	163.24(18)	N(3)-Cd(2)-O(6)	86.72(19)
N(6)#1-Cd(2)-O(6)	89.2(2)	N(6)#1-Cd(2)-O(10)#1	91.59(19)
O(6)-Cd(2)-O(9)#1	134.39(16)	N(3)-Cd(2)-O(10)#1	94.24(18)
O(6)-Cd(2)-O(10)#1	173.56(15)	O(9)#1-Cd(2)-Cl(2)	137.86(12)
O(9)#1-Cd(2)-O(10)#1	52.05(15)	O(10)#1-Cd(2)-Cl(2)	85.87(11)
N(6)#1-Cd(2)-O(5)	84.04(17)	N(3)-Cd(2)-O(5)	80.54(16)
O(9)#1-Cd(2)-O(5)	81.44(15)	O(10)#1-Cd(2)-O(5)	133.49(14)
Cl(2)-Cd(2)-O(5)	140.58(10)	N(5)-Cd(3)-Cl(3)	98.97(12)
N(7)-Cd(3)-N(5)	161.99(16)	N(7)-Cd(3)-O(4)	87.33(17)
N(5)-Cd(3)-O(4)	86.11(17)	N(7)-Cd(3)-O(12)	96.35(17)
N(5)-Cd(3)-O(12)	91.88(16)	N(7)-Cd(3)-Cl(3)	97.63(12)
O(4)-Cd(3)-O(12)	173.51(15)	O(4)-Cd(3)-Cl(3)	88.70(12)
O(4)-Cd(3)-O(3)	51.84(16)	N(5)-Cd(3)-O(3)	82.71(16)
N(7)-Cd(3)-O(3)	80.05(16)	O(12)-Cd(3)-Cl(3)	85.51(11)
O(12)-Cd(3)-O(11)	52.49(15)	N(7)-Cd(3)-O(11)	83.53(17)
Cl(3)-Cd(3)-O(11)	137.63(11)	N(5)-Cd(3)-O(11)	88.89(16)
O(3)-Cd(3)-O(11)	81.69(16)	O(4)-Cd(3)-O(11)	133.53(15)
Cl(3)-Cd(3)-O(3)	140.46(13)	O(12)-Cd(3)-O(3)	134.03(16)

O(3W)-Cd(4)-O(3W)#2	180.0	O(2W)#2-Cd(4)-O(3W)#2	93.73(17)
O(2W)-Cd(4)-O(3W)#2	86.27(17)	O(1W)-Cd(4)-O(3W)#2	95.99(17)
O(1W)#2-Cd(4)-O(3W)#2	84.01(17)	O(2W)-Cd(4)-O(3W)	93.73(17)
O(2W)#2-Cd(4)-O(3W)	86.27(17)	O(1W)#2-Cd(4)-O(2W)	95.25(17)
O(1W)-Cd(4)-O(3W)	84.01(17)	O(1W)#2-Cd(4)-O(3W)	95.99(17)
O(1W)-Cd(4)-O(2W)#2	95.25(17)	O(2W)-Cd(4)-O(2W)#2	180.0
O(1W)- Cd(4)-O(2W)	84.75(17)	O(1W)#2-Cd(4)-O(2W)#2	84.75(17)
O(1W)#2-Cd(4)-O(1W)	180.0		

Compound **4**

Hg(1)-S(1)	2.325(2)	Hg(1)-S(2)	2.327(2)
Cd(1)-Cl(1)	2.4426(19)	Cd(1)-Cl(2)	2.4644(19)
Cd(1)-Cl(3)	2.4644(19)	Cd(1)-Cl(4)	2.452(2)
S(1)-Hg(1)-S(2)	171.58(6)	Cl(1)-Cd(1)-Cl(2)	110.97(7)
Cl(1)-Cd(1)-Cl(3)	114.15(6)	Cl(1)-Cd(1)-Cl(4)	105.49(7)
Cl(2)-Cd(1)-Cl(3)	105.37(7)	Cl(2)-Cd(1)-Cl(4)	106.11(8)
Cl(3)-Cd(1)-Cl(4)	114.54(8)		

Table S3 The hydrogen bonding parameters (Å, º) between the coordinated water in $[Cd(H_2O)_6]^{2+}$ and carboxylate oxygen atom in **3**

D–H···A	D–H	H···A	D···A	D–H···A
O1W-H1X···O5	0.96	2.04	2.717(6)	126.0
O1W-H1Y···O2	0.96	1.91	2.728(7)	141.9
O2W-H2X···O11	0.96	1.91	2.700(6)	137.9
O2W-H2Y···O8^{i}	0.96	1.81	2.754(6)	165.7
O3W-H3X···O9	0.96	1.87	2.793(6)	159.3
O3W-H3Y···O8	0.96	2.54	3.414(7)	150.7
O6W-H6X···O16	0.83	1.96	2.317(6)	104.7
O6W-H6Y···O16^{ii}	0.83	1.99	2.317(6)	102.4
O6W-H6Y···N12^{ii}	0.83	2.51	3.311(7)	164.0

Symmetry codes: (i) 2–*x*, 2–*y*, 2– *z*; (ii) 2–*x*, 2–*y*, 1– *z*.

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