Supporting Information

New Mercury-Contained Cationic Frameworks Stabilized by $(GaCl_4)^-$ Unit via Weak Electrostatic Forces in Supramolecular Complexes $(Hg_{11}P_4)(GaCl_4)_4$ and $(Hg_3AsS)(GaCl_4)$

*Xiao-Ming Jiang, Xiao-Guo Li, Yu-Hang Fan, Bin-Wen Liu, Hui-Yi Zeng, Guo-Cong Guo**

Table S1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **1** and **2**.

Atom	x	y	z	$U_{(eq)}$[a] ($Å^2$)	Occupancy	Wyckoff
1						
Hg(1)	0.74481(11)	0.0000	0.21903(6)	0.0385(4)	1	4i
Hg(2)	0.52172(11)	0.0000	0.05913(6)	0.0437(4)	1	4i
Hg(3)	0.49425(8)	0.25054(14)	0.21976(4)	0.0385(3)	1	8j
Hg(4)	0.96165(15)	0.0000	0.38109(7)	0.0740(7)	1	4i
Hg(5)	1.0000	0.0000	0.5000	0.1169(14)	1	2c
Ga(1)	0.6309(3)	0.0000	0.38801(16)	0.0417(11)	1	4i
Ga(2)	1.2124(3)	0.0000	0.11616(17)	0.0400(10)	1	4i
P(1)	0.5619(7)	0.0000	0.1719(4)	0.035(2)	1	4i
P(2)	0.9258(7)	0.0000	0.2688(3)	0.031(2)	1	4i
Cl(1)	1.2439(7)	0.0000	0.2165(4)	0.041(2)	1	4i
Cl(2)	1.0400(7)	0.0000	0.0841(5)	0.065(3)	1	4i
Cl(3)	0.6972(6)	0.2363(10)	0.3481(3)	0.064(2)	1	8j
Cl(4)	0.4620(7)	0.0000	0.3484(5)	0.067(3)	1	4i

Cl(5)	1.2830(6)	0.2427(9)	0.0848(3)	0.065(2)	1	8j
Cl(6)	0.6610(12)	0.0000	0.4862(5)	0.114(5)	1	4i
2						
Hg(1)	0.50178(5)	0.00355(10)	0.04170(8)	0.0338(3)	1	6c
Ga(1)	0.0000	0.0000	0.2447(3)	0.0188(8)	1	2a
As(1)	0.6667	0.3333	-0.0572(7)	0.0336(16)	0.776(12)	2b
S(1)	0.3333	-0.3333	0.1562(9)	0.0199(17)	1	2b
Cl(1)	0.3314(7)	0.1657(4)	0.2907(10)	0.0327(9)	1	6c
Cl(2)	0.0000	0.0000	0.0572(6)	0.023(2)	1	2a
As(2)	0.6667	0.3333	-0.208(4)	0.046(6)	0.224(12)	2b

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Select bond distances lengths (Å)[a] for **1** and **2**.

bond	distance	bond	distance
1			
Hg(1)-P(2)	2.373(8)	Ga(1)-Cl(4)	2.176(10)
Hg(1)-P(1)	2.379(9)	Ga(1)-Cl(3)#4	2.185(7)
Hg(2)-P(1)	2.446(8)	Ga(1)-Cl(3)	2.185(7)
Hg(2)-Hg(2)#1	2.566(3)	Ga(2)-Cl(5)#4	2.167(7)
Hg(3)-P(1)	2.362(5)	Ga(2)-Cl(5)	2.167(7)
Hg(3)-P(2)#2	2.373(5)	Ga(2)-Cl(1)	2.175(8)
Hg(4)-P(2)	2.435(8)	Ga(2)-Cl(2)	2.187(9)
Hg(4)-Hg(5)	2.5783(17)	P(1)-Hg(3)#4	2.362(5)
Hg(5)-Hg(4)#3	2.5783(17)	P(2)-Hg(3)#5	2.373(5)
Ga(1)-Cl(6)	2.130(11)	P(2)-Hg(3)#6	2.373(5)
2			

Hg(1)-As(1)	2.383(4)	Ga(1)-Cl(2)	2.243(10)
Hg(1)-S(1)	2.519(6)	As(1)-Hg(1)#3	2.383(4)
Ga(1)-Cl(1)	2.151(5)	As(1)-Hg(1)#4	2.383(4)
Ga(1)-Cl(1)#1	2.151(5)	S(1)-Hg(1)#5	2.519(6)
Ga(1)-Cl(1)#2	2.151(5)	S(1)-Hg(1)#6	2.519(6)

[a] Symmetry codes. Compound **1**: (#1) -x+1,-y,-z; (#2) x-1/2,y+1/2,z; (#3) -x+2,-y,-z+1; (#4) x,-y,z; (#5) x+1/2,y-1/2,z; (#6) x+1/2,-y+1/2,z. Compound **2**: (#1) -x+y,-x,z; (#2) -y,x-y,z; (#3) -y+1,x-y,z; (#4) -x+y+1,-x+1,z; (#5) -y,x-y-1,z; (#6) -x+y+1,-x,z.

Table S3. The state energies (eV) of the lowest conduction band (L-CB) and the higest valence band (H-VB) at some *k*-points in the Brillouin-zone of **1** and **2**.

k-point	H-VB	L-CB
	1	
L(-0.5, 0.0, 0.5)	-0.005864	2.580483
M(-0.5, -0.5, 0.5)	-0.001548	2.546894
A(-0.5, 0.0, 0.0)	0	2.586634
G(0.0, 0.0, 0.0)	-0.365405	2.125357
Z(0.0, -0.5, 0.5)	-0.005872	2.580482
V(0.0, 0.0, 0.5)	-0.318718	1.938842
	2	
A(0.0, 0.0, 0.5)	-0.753964	2.962441
H(-0.333, 0.667, 0.5)	-0.040327	3.29565
K(-0.333, 0.667, 0.0)	-0.01602043	3.204896
G(0.0, 0.0, 0.0)	-0.205108	2.467778
M(0.0, 0.5, 0.0)	-0.015783	3.04015
L(0.0, 0.5, 0.5)	-0.079863	3.170191

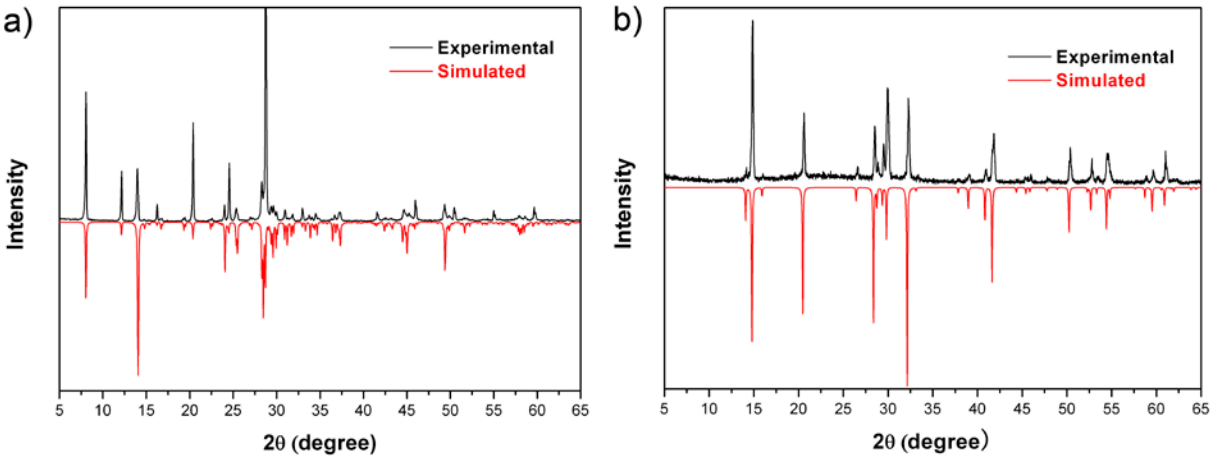

Figure S1: Simulated and experimental (~293K) XRD powder patterns of **1** (a) and **2** (b). The two compounds can be easily cleaved along the crystallographic *c* direction during grinding. When the powder samples for the XRD measurement were ground and deposited on a glass slide, the crystals tend to lie on some faces. Intensities of some minor peaks on the experimental patterns don't match those on the simulated ones because of the effect of preferred orientation.

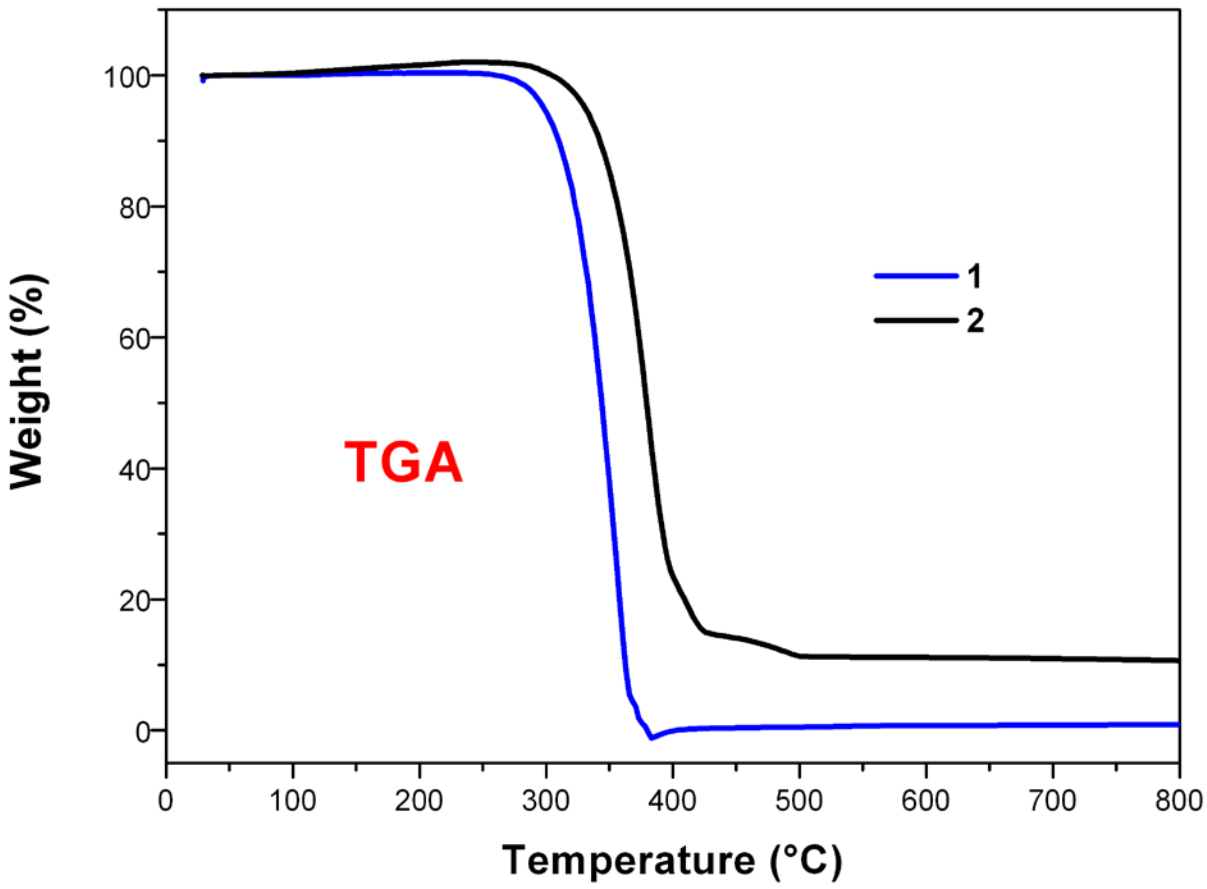

Figure S2: TGA curves for **1** and **2**.

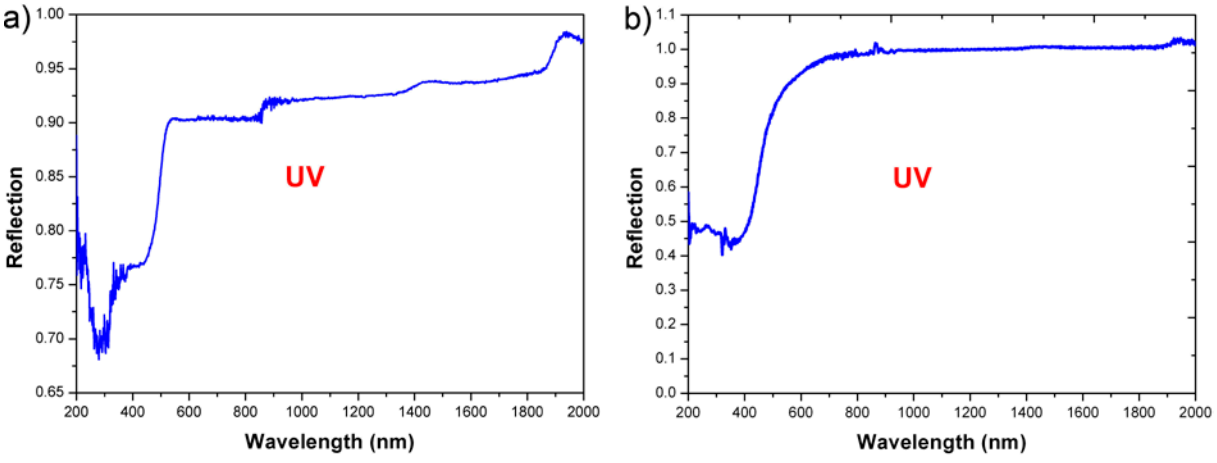

Figure S3: UV diffuse reflectance spectra of **1** (a) and **2** (b).

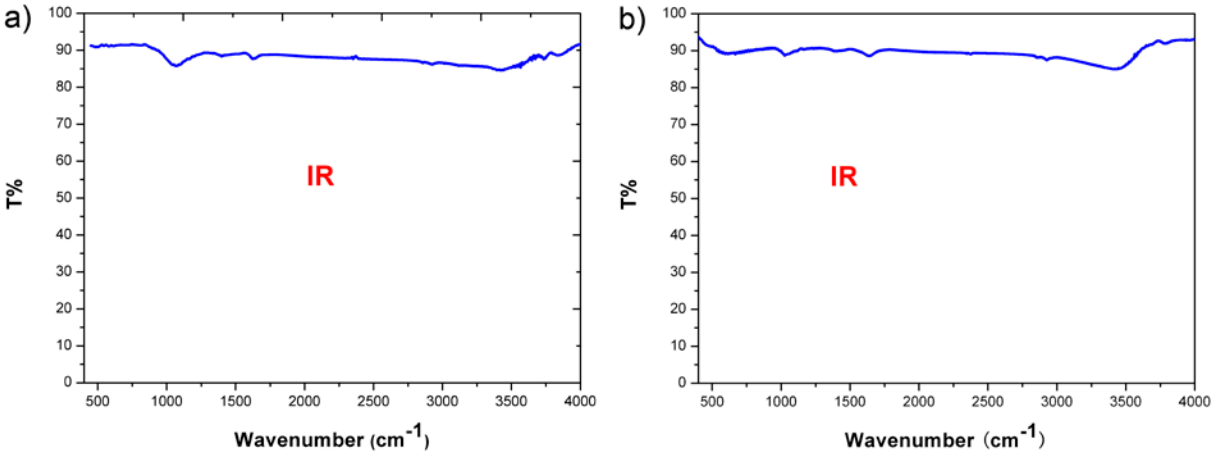

Figure S4: FT-IR spectra of **1** (a) and **2** (b). The minor peaks at ~920, ~1640, and ~3300 cm^{-1} can be attributed to water.