Electronic Supporting Information for:

A nano-scale triangular ring cluster of indium-selenide: structure and templating effect

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1. Experimental Section

Synthesis of compound 2. The crystals 2 were synthesized from elemental Mn (0.0014 g, 0.025 mmol), $InCl_3$ (0.012g,0.05mmol), Se (0.0016g, 0.10 mmol) and (BMIm)Br (25 mg, 0.114 mmol) in a water solution of 1 mL 85% dach. The mixture was heated to 140℃ for 10 days in a sealed thick-walled Pyrex tube with an inner volume of 12 mL. After cooling to room temperature the block yellow crystals were obtained with 76% yield (based on In). Elemental analysis calcd. For $C_{444}H_{1061}Cl_9In_{84}Mn_{23}N_{148}O_7Se_{150}$ (FW 31658.83): C, 16.84; H, 3.38; N, 6.55%. Found: C, 16.68; H, 3.35; N, 6.27%. IR data (KBr, cm21): 3446(s), 3218(m), 2924(s), 2852(m), 1636(m), 1575(s), 1448(m), 1396(w), 1118(w), 1025(s), 769(w).

X-ray Crystallography. The X-ray crystallographic data of **2** was carried out on Rigaku Mercury diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The structure was solved by direct method using SHELXS-2014 and the refinement against all reflections of the compound was performed using SHELXL-2014. Crystal data are available and have been deposited to the CCDC data center (CCDC 1059898), though the data are still not satisfying due to their large volume (162764) and disorder. However, the anion structures are accurately solved. Relevant crystal data, collection parameters, and refinement results can be found in Table S1.

The ordinary bond distances of In–Se of **2** are 2.518(6)–2.658(4) Å for tetrahedral In atoms and 2.519(4)–2.855(4) Å for trigonal-bipyramid In8 and In11, which are chelated by a dach with In–N distances of 2.23(3)–2.46(3) Å. The longer In–Se distances over 2.7 Å are attributed to the weak bonding of the tetrahedral and triangle bridged Se13 and Se19 atoms, respectively. The Mn–Se distances are 2.671(5)–2.739(5) Å and the Mn–N bond distances are 2.24(2)–2.38(2) Å.

2. SI Figures

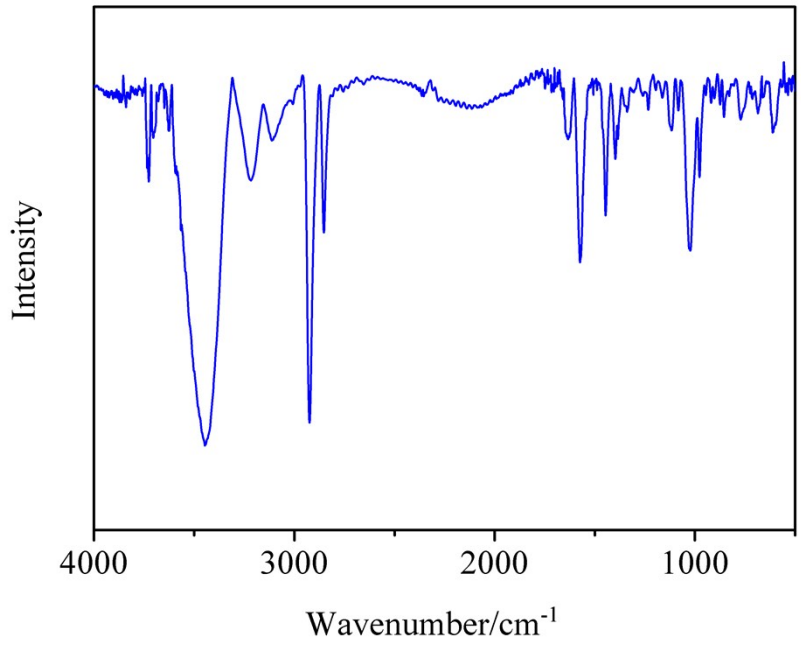


Figure S1. FTIR spectrum of compound 2.

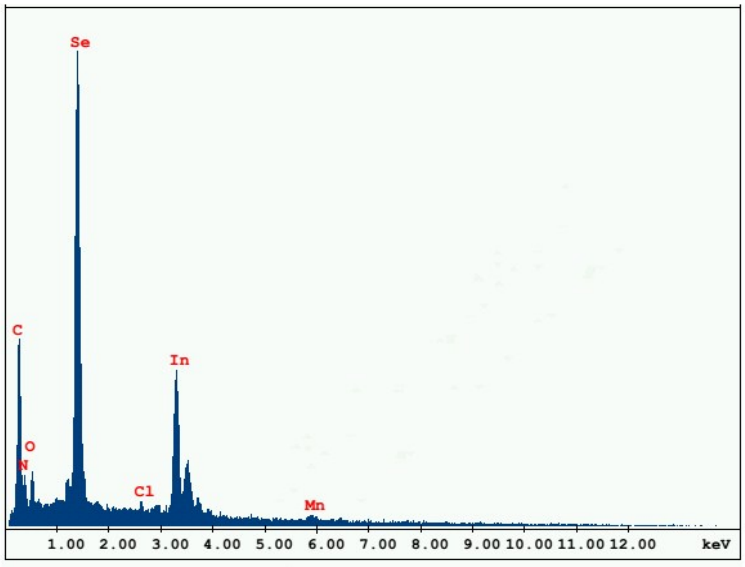


Figure S2. EDS result of compound 2.

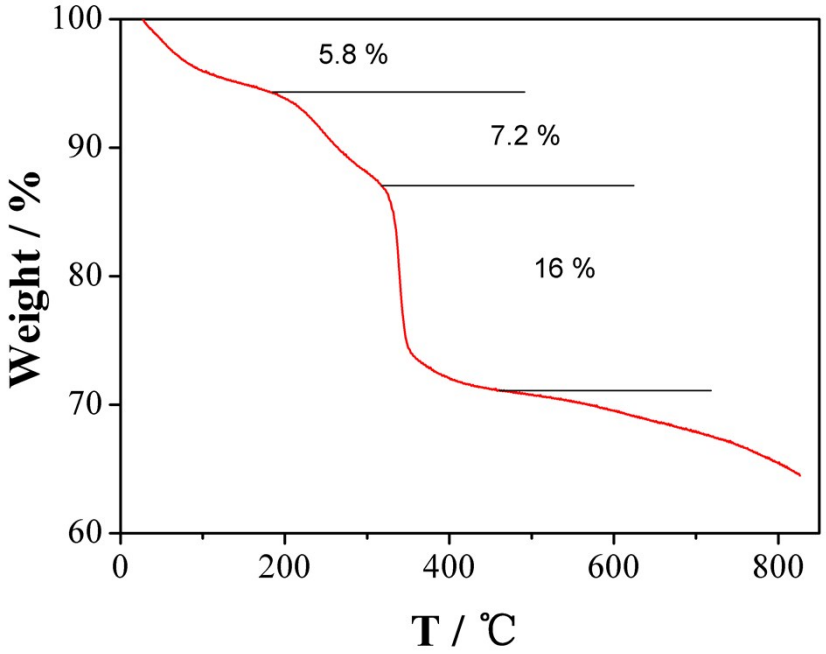


Figure S3. Thermogravimetric measurement of compound 2.

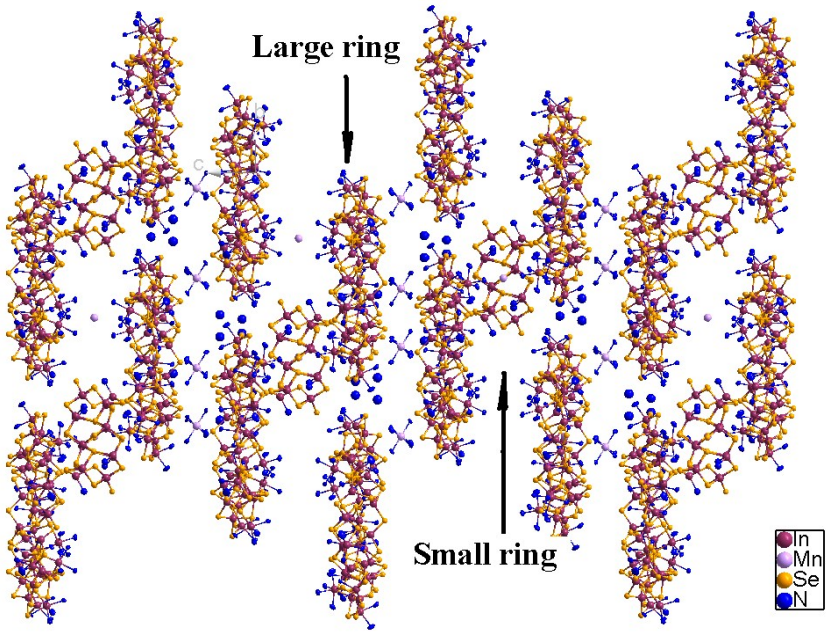
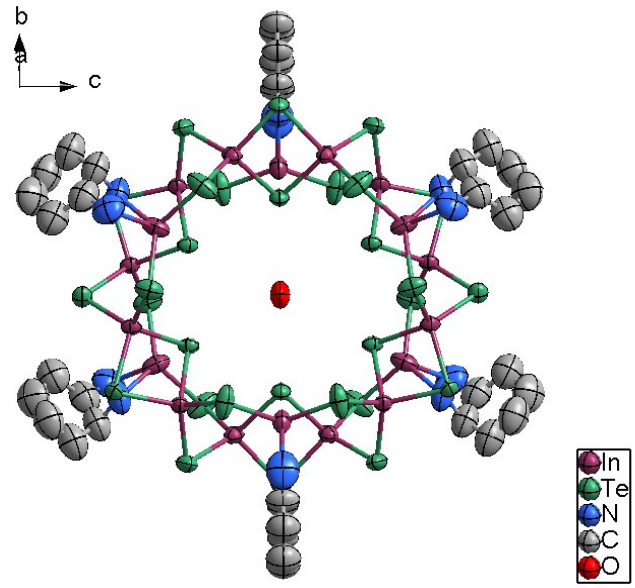
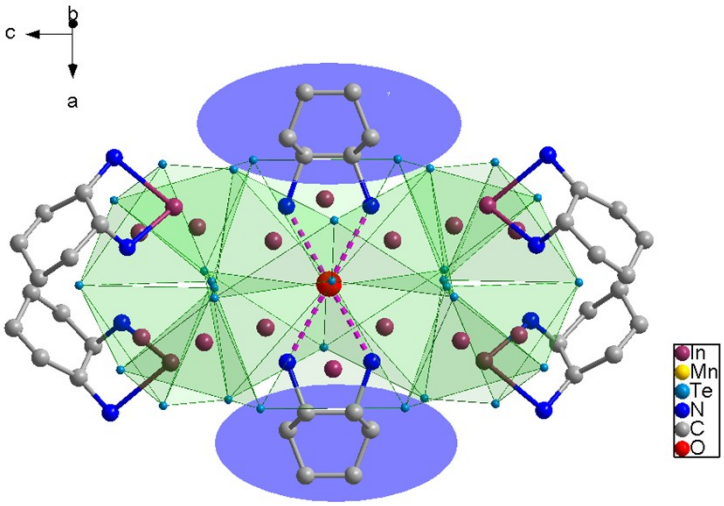


Figure S4. The anion packing of 2, showing the arrangement of large rings and small rings in 2:1 ratio.



(a)



(b)

Figure S5. (a) Structure of the small circular ring. (b) Templating effect of the $[H_2O(Hdach)_2]^{2+}$ on the formation of small ring.

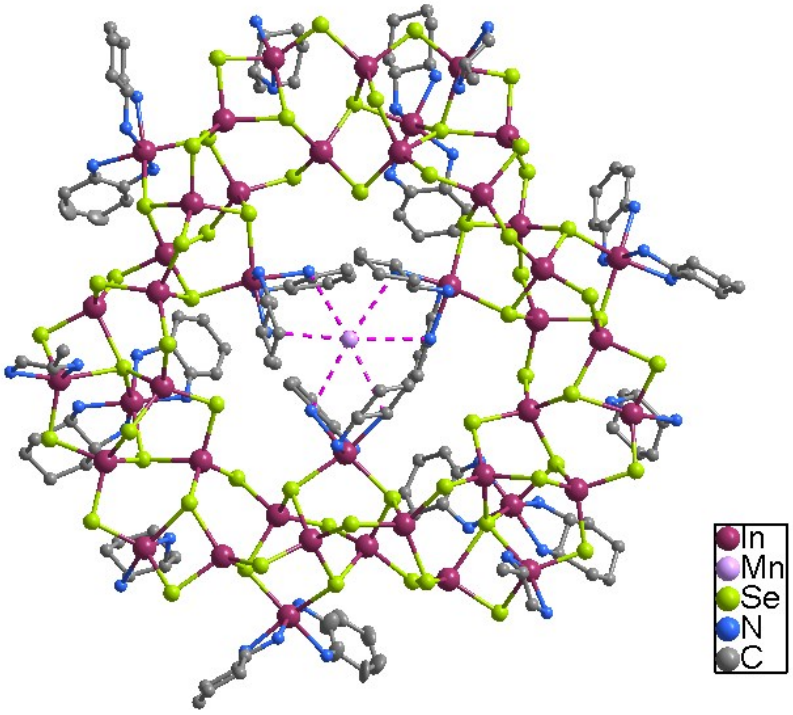


Figure S6. The $[Mn(dach)_2]^{2+}/Mn^{2+}$ second sphere coordination templating effect on the formation of large triangular ring.

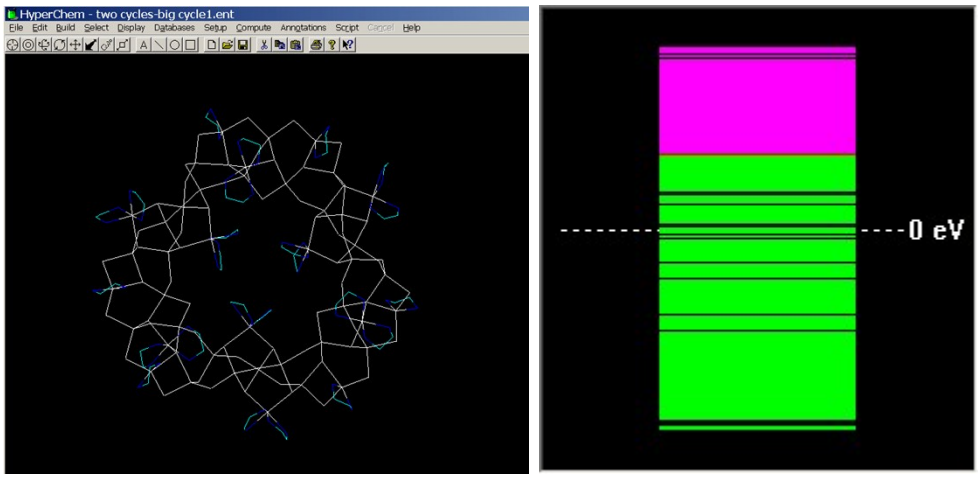


Figure S7. A preliminary culculation using HyperChem (semi-empirical) indicates the dense band structure of the InSeMn ring.

3. SI Table

Table S1. Crystal Data and Structural Refinement Parameters for compound **2.**

	2
formula	$C_{444}H_{1061}Cl_9In_{84}Mn_{23}N_{148}O_7Se_{150}$
Fw	31658.89
cryst size (mm^3)	0.50 × 0.35 × 0.10
cryst syst	trigonal
space group	*R*-3*c*
a (Å)	34.7264(6)
b (Å)	34.7264(6)
c (Å)	155.851(3)
α (deg)	90.00
β (deg)	90.00
γ (deg)	120.00
V ($Å^3$)	162764(6)
Z	6
ρ_{calcd} ($g\ cm^{-3}$)	1.938
F(000)	88566
μ (mm^{-1})	7.092
T (K)	293(2)
reflns collected	314111
unique reflns	16330
observed reflns	12236
no. params	1214
restraints	392
GOF on F^2	1.167
R_1[I>2σ(*I*)]	0.0985
$_wR_2$[I>2σ(*I*)]	0.1940