

Supporting Information

Polyoxometalate-incorporated Metallapillararene/Metallacalixarene Metal-organic frameworks as Anode Materials for Lithium-ion Batteries

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Contents

- 1. The molecular structure unit for 1-4. (Figure S1)**
- 2. Additional structural figures for 1. (Figure S2-4)**
- 3. Additional structural figures for 2. (Figure S4-6)**
- 4. Additional physical characterization for compounds 1-4. (Figure S7-10)**
- 5. The electrochemistry performances of POM-based crystal compounds with different structures and components as anode materials. (Table S1)**
- 6. Additional physical characterization and data for compounds as anode material. (Table S2 and Figure S11)**
- 7. Bond lengths and angles for compounds 1-4. (Table S3-6)**

1. The molecular structure unit for 1-4.

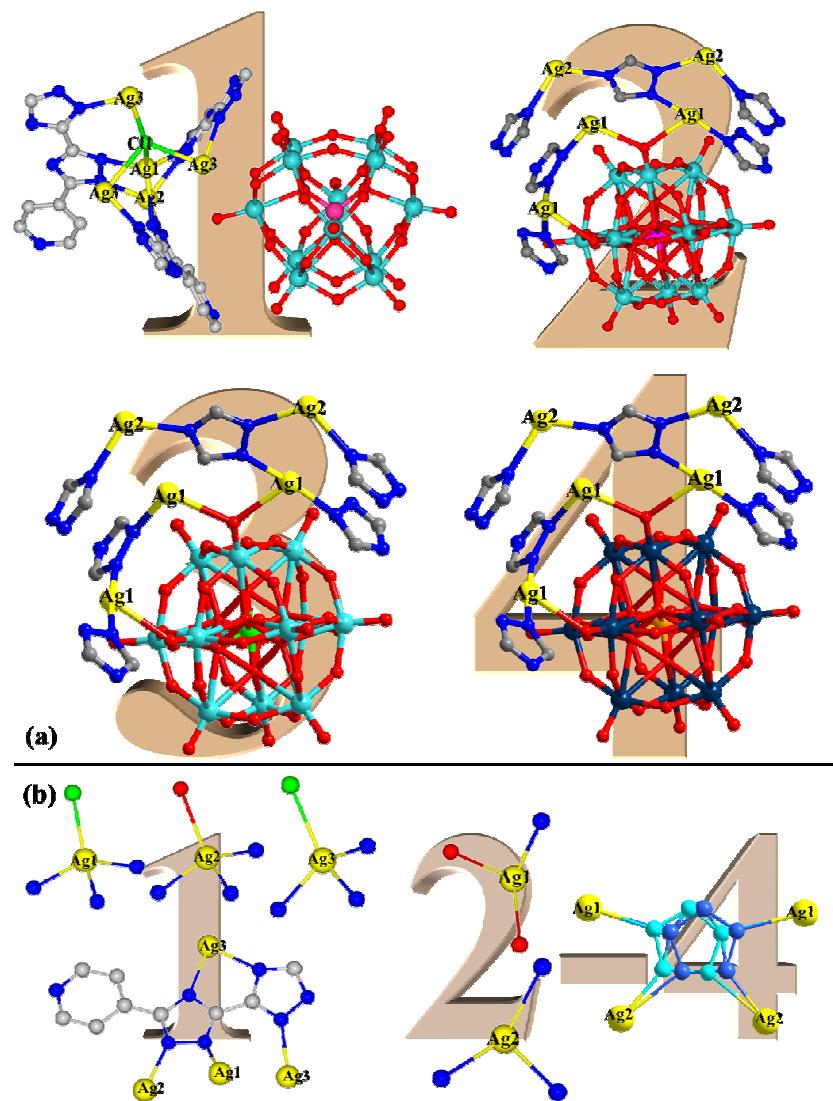


Figure S1 (a) Combined ball and stick representation of the molecular structure unit of compounds **1-4**. All the hydrogen and water atoms have been omitted for clarity. (b) Combined ball/stick representation of coordination information of Ag ions and organic ligand (pyttz for **1** and trz for **2-4**) in compounds **1-4**.

2. Additional structural figures for 1.

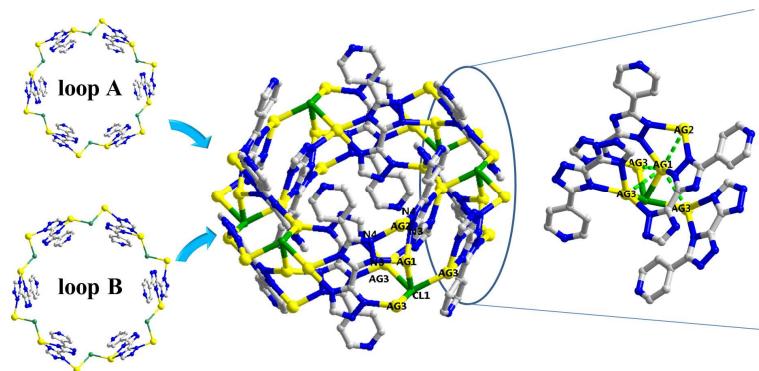


Figure S2 Ball/stick representation of the double layer metallapillar[6]-arene constructed by loop A and B.(left) Combined ball and stick representation of argentophilic Ag^+ - Ag^+ interactions.(right)

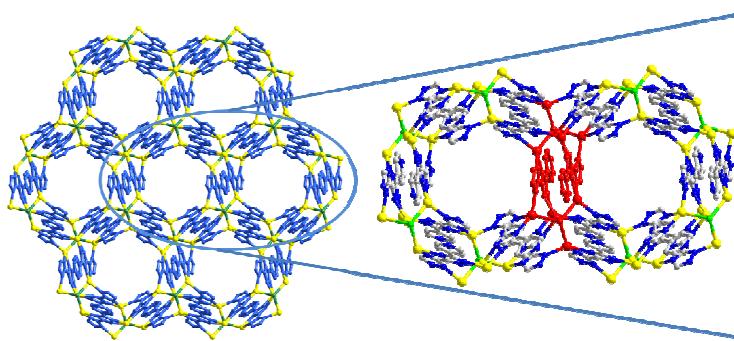


Figure S3 Ball/stick representation the 2D pillararene -like array constructed the metallapillararene building block by sharing the sides of the inner and outer loops.

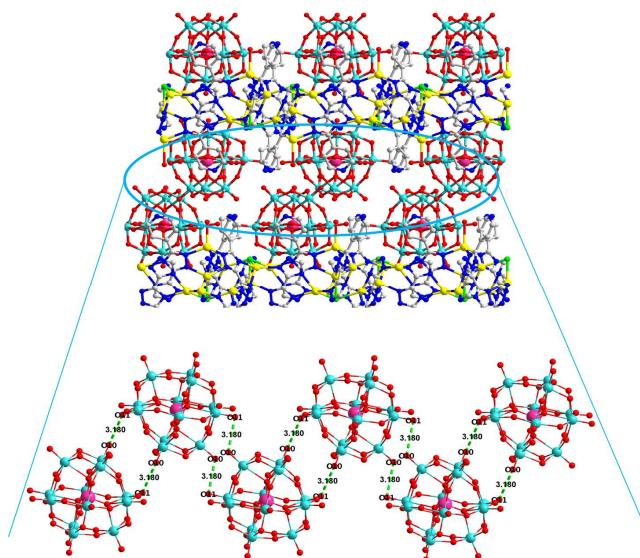


Figure S4 Ball/stick representation of 3D supramolecular structure constructed by 2D POM-metallapillararene layers *via* the short interaction among the POMs.

3. Additional structural figures for 2.

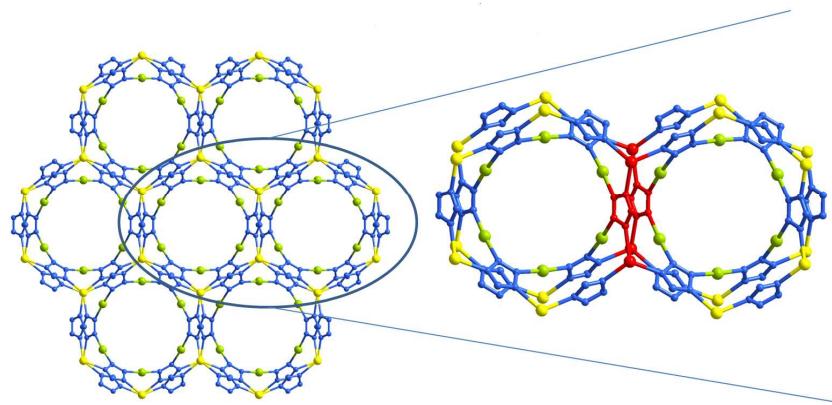


Figure S5 Ball/stick representation the 2D calixarene-like array constructed by metallacalix[6]-arenes unit by sharing a side of itself.

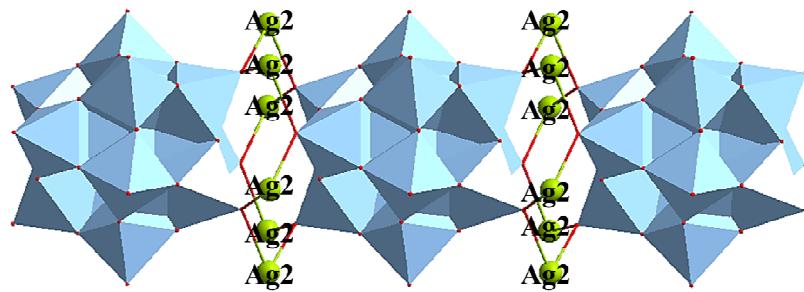


Figure S6 Ball/stick/polyhedral representation of the 1D inorganic chains constructed by POMs and Ag ions.

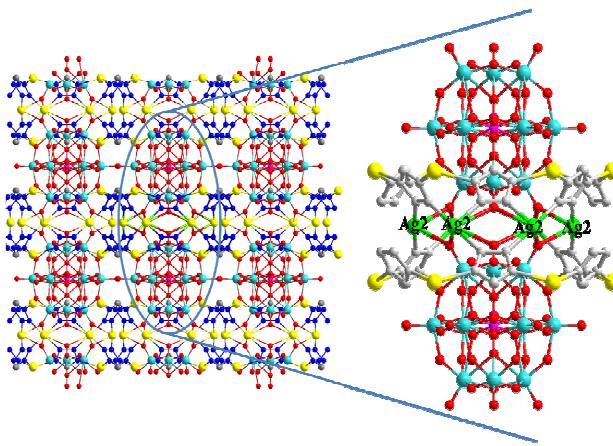


Figure S7 Ball/stick representation of 3D structure constructed by the POM-Ag 1D chains and 2D [Ag₂(trz)₃]_n networks *via* Ag-O bonds.

4. Additional physical characterization for compound 1-4.

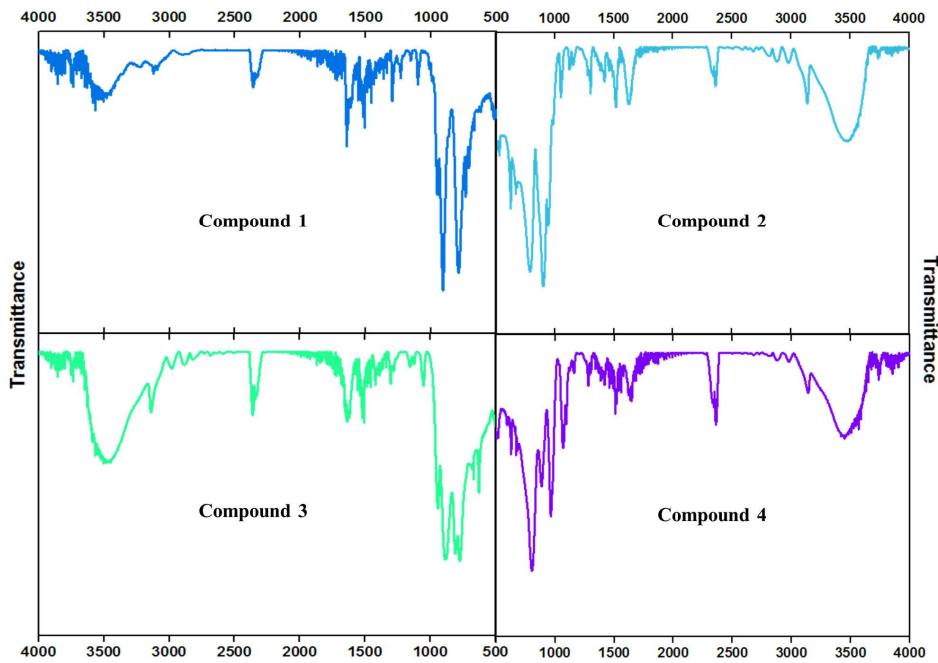


Figure S8 IR spectra of compounds 1-4.

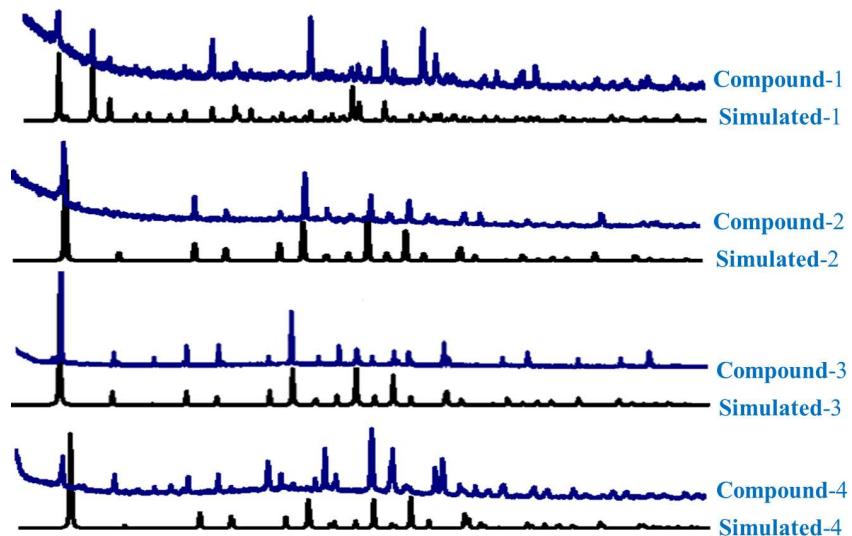


Figure S9 The simulated and experimental PXRD patterns of compounds 1-4 in 2θ range of 5 – 50°.

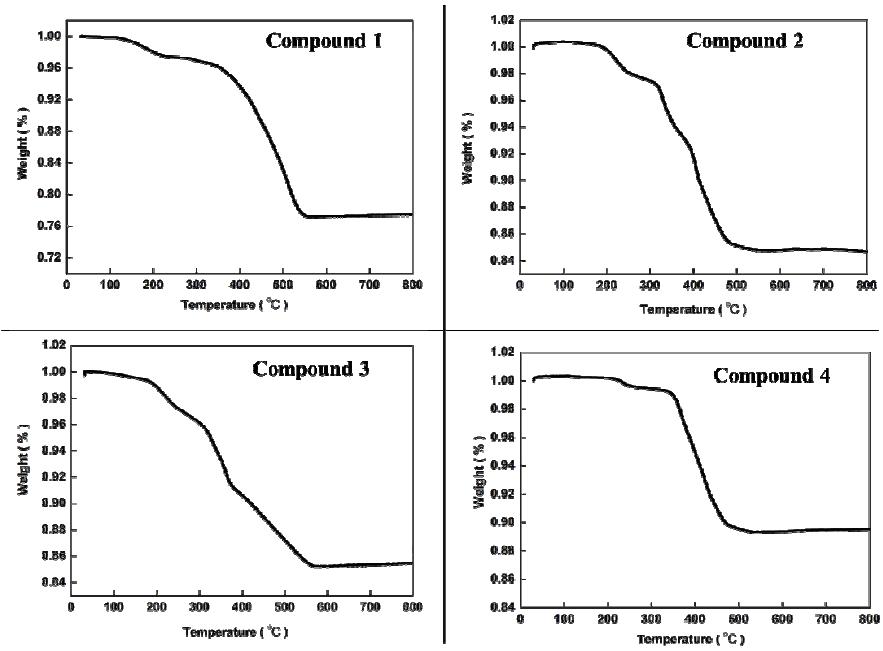


Figure S10 The TGA curve of compounds 1-4.

5. The electrochemistry performances of POM-based crystal compounds with different structures and components as anode materials.

Table S1 The electrochemistry performances of POM-based crystal compounds as anode materials.

Compound	First discharge capacity (mAh g ⁻¹)	Stable discharge capacity (mAh g ⁻¹)	current density (mA g ⁻¹)	Ref
[Ag ₅ (pytz) ₃ Cl·(H ₂ O)][H ₅ SiMo ₁₂ O ₄₀]·3H ₂ O	1344	520	100	This work
[Ag ₅ (trz) ₆][H ₅ SiMo ₁₂ O ₄₀]	1452	570	100	This work
[Ag ₂₆ (Trz) ₁₆ (OH) ₄][P ₂ W ₁₈ O ₆₂]	1077	400	100 mA cm ⁻²	[1]
Na[Ag ₁₆ (Trz) ₉ (H ₂ O) ₄][P ₂ W ₁₈ O ₆₂]·H ₂ O	1094	400	100 mA cm ⁻²	[1]
{[Ni ₆ (OH) ₃ (H ₂ O)(en) ₃ (PW ₉ O ₃₄)][Ni ₆ (OH) ₃ (H ₂ O) ₄ (en) ₃ (PW ₉ O ₃₄)](BDC) _{1.5} } [Ni(en)(H ₂ O) ₄]	1525	540	0.25 C	[2]

References

- [1] Li, M. T.; Cong, L.; Zhao, J.; Zheng, T. T.; Tian, R.; Sha, J. Q.; Su Z. M.; Wang, X. L., *J. Mater. Chem. A* **2017**, *5*, 3371-3376.
- [2] Yue, Y.; Li, Y.; Bi, Z.; Veith, G. M.; Bridges, C. A.; Guo, B.; Chen, J.; Mullins, D. R.; Surwade, S. P.; Mahurin , S. M.; Liu, H.; Parans Paranthaman, M.; Dai, S.; *J. Mater. Chem. A*, **2015**, *3*, 22989-22995.

6. Additional physical characterization and data for compounds as anode material.

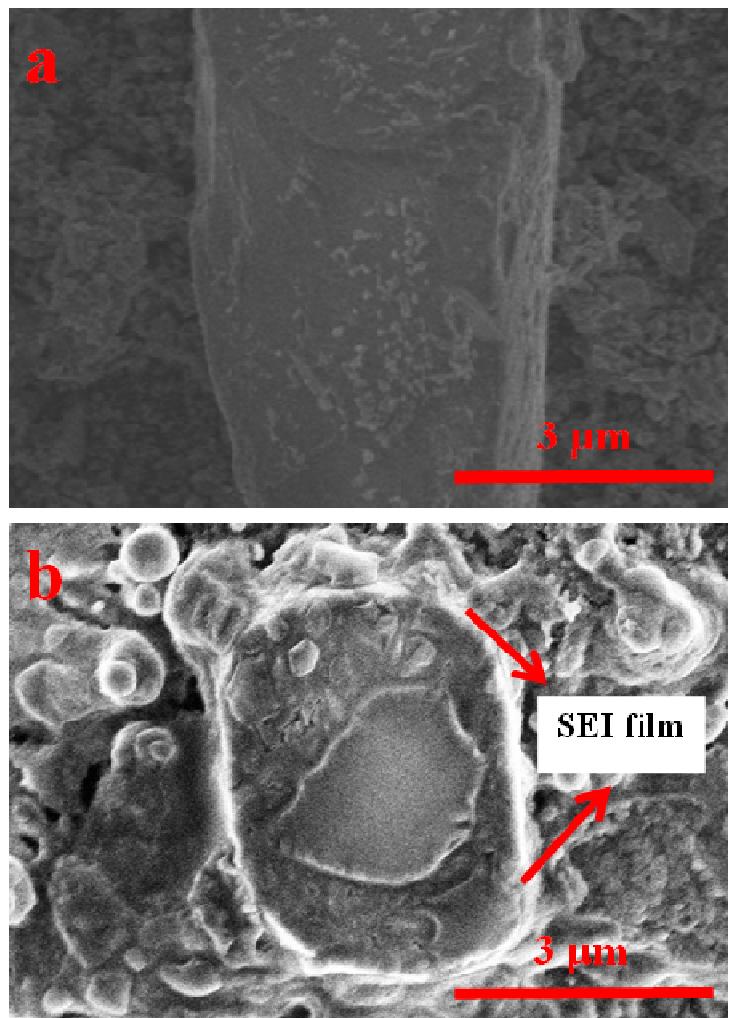


Figure S11. SEM images before (a) and after test (b) of the compound 2

Table S2 The fitting errors of the simulated equivalent circuit of **1** and **2** anodes

	Compound 1	Compound 2
$R_{\text{e}} (\Omega)$	5.36	5.89
$R_{\text{f}} (\Omega)$	21.03	27.49
$R_{\text{ct}} (\Omega)$	88.16	53.76
Sum (Ω)	114.55	87.14

O(2)-W(1)-O(1)	156.0(7)	N(3)-N(1)-Ag(2)	161(5)
O(3)-W(1)-O(1)#4	102.9(7)	C(2)-N(1)-Ag(2)	120(2)
O(2)#8-W(1)-O(1)#4	156.0(7)	N(2)-N(1)-Ag(2)	141.1(17)
O(2)-W(1)-O(1)#4	87.8(6)	C(1)-N(1)-Ag(2)	137.2(17)
O(1)-W(1)-O(1)#4	87.2(7)	N(1)-N(3)-C(2)	92(5)
O(3)-W(1)-O(6)	159.2(7)	N(1)-N(3)-N(2)	123(5)
O(2)#8-W(1)-O(6)	93.9(6)	C(2)-N(3)-N(2)	30.7(14)
O(2)-W(1)-O(6)	93.9(6)	N(1)-N(3)-C(1)	121(5)
O(1)-W(1)-O(6)	63.1(6)	C(2)-N(3)-C(1)	141(3)
O(1)#4-W(1)-O(6)	63.1(6)	N(2)-N(3)-C(1)	112(3)
O(3)-W(1)-O(7)	158.7(6)	N(2)-C(2)-N(3)	79(3)
O(2)#8-W(1)-O(7)	64.3(4)	N(2)-C(2)-N(1)	105(4)
O(2)-W(1)-O(7)	64.3(4)	N(3)-C(2)-N(1)	25.2(15)
O(1)-W(1)-O(7)	92.5(7)	N(2)-C(2)-Ag(1)	128(4)
O(1)#4-W(1)-O(7)	92.5(7)	N(3)-C(2)-Ag(1)	151(2)
O(6)-W(1)-O(7)	42.1(6)	N(1)-C(2)-Ag(1)	127(2)
O(5)-W(2)-O(4)#9	101.7(6)	C(2)-N(2)-N(3)	70(3)
O(5)-W(2)-O(4)#3	101.7(6)	C(2)-N(2)-N(1)	53(3)
O(4)#9-W(2)-O(4)#3	156.7(11)	N(3)-N(2)-N(1)	17.1(15)
O(5)-W(2)-O(2)#9	101.6(4)	C(2)-N(2)-Ag(1)	41(3)
O(4)#9-W(2)-O(2)#9	87.0(4)	N(3)-N(2)-Ag(1)	110(2)
O(4)#3-W(2)-O(2)#9	88.3(5)	N(1)-N(2)-Ag(1)	93.1(15)
O(5)-W(2)-O(2)#10	101.6(4)	N(3)-C(1)-N(1)	16.8(14)
O(4)#9-W(2)-O(2)#10	88.3(5)	O(2)#9-W(2)-O(7)#9	64.1(5)
O(4)#3-W(2)-O(2)#10	87.0(4)	O(2)#10-W(2)-O(7)#9	93.5(5)
O(2)#9-W(2)-O(2)#10	156.7(8)	O(5)-W(2)-O(7)#3	159.2(3)
O(5)-W(2)-O(7)#9	159.2(3)	O(4)#9-W(2)-O(7)#3	93.3(7)
O(4)#9-W(2)-O(7)#9	64.2(6)	O(4)#3-W(2)-O(7)#3	64.2(6)
O(4)#3-W(2)-O(7)#9	93.3(7)	O(2)#9-W(2)-O(7)#3	93.5(5)
O(7)#9-W(2)-O(7)#3	41.7(6)	O(2)#10-W(2)-O(7)#3	64.1(5)

Symmetry transformations used to generate equivalent atoms: #1 -x+y+1,-x+2,z; #2 -x+y,-x+1,z; #3 -x+1,-y+2,-z+1; #4 -y+2,x-y+1,z; #5 y,-x+y+1,-z+1; #6 x-y+1,x,-z+1; #7 -x+2,-y+2,-z+1; #8 x-y+1,-y+2,z; #9 -y+1,x-y+1,z; #10 -x+y,y,-z+1