Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

Polyoxometalate-directed two 3D metal-organic frameworks with multinuclear silver-ptz cycle/belts as subunits†

Xiuli Wang,* Na Li, Aixiang Tian, Jun Ying, Guocheng Liu, Hongyan Lin, Yang Yang

Synthesis of $[Ag_7(ptz)_4][PW_{12}O_{40}]\cdot 4H_2O$ (3)

Compound **3** was prepared in the same way as **2** except that $H_3PW_{12}O_{40}\cdot xH_2O$ (0.1 g, 0.035 mmol) was used instead of $H_3PMo_{12}O_{40}\cdot xH_2O$ and the pH value was adjusted to about 2.3. Dark red block crystals of **3** were obtained. Yield 50% based on W.

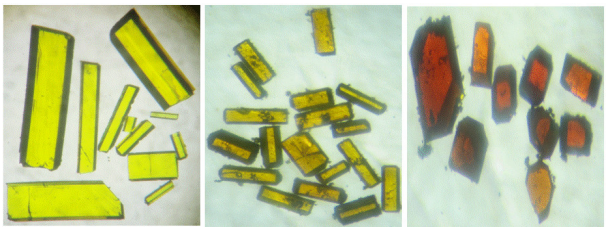

Fig. S1 The photograph of compounds **1–3** (left: compound **1**, middle: compound **2**, right: compound **3**).

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

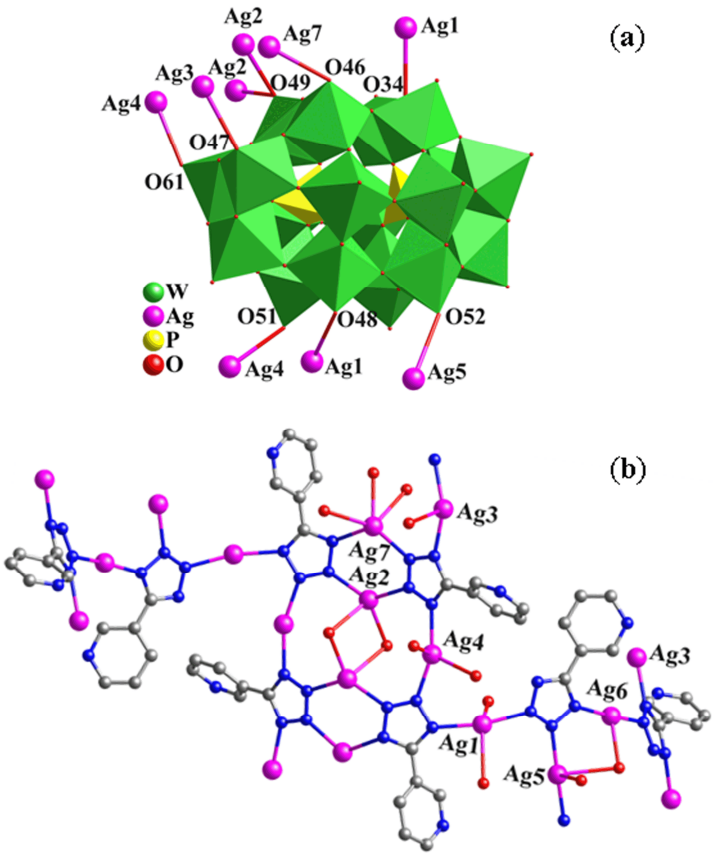

Fig. S2 (a) The coordination environment of P_2W_{18} polyoxoanion. (b) The coordination modes of Ag^I ions and ptz ligands in compound **1**. The crystal water and hydrogen atoms are omitted for clarity.

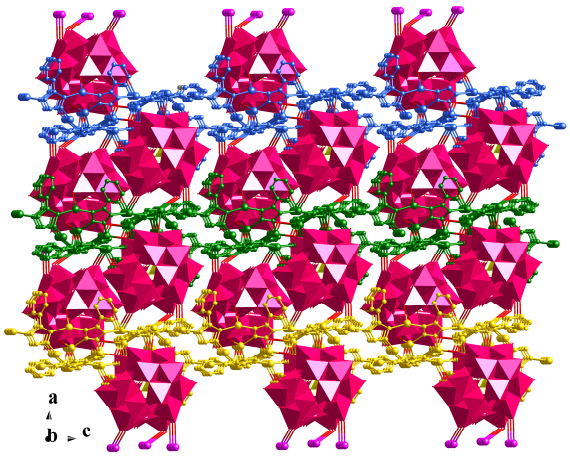

Fig. S3 The 3D framework of **1**.

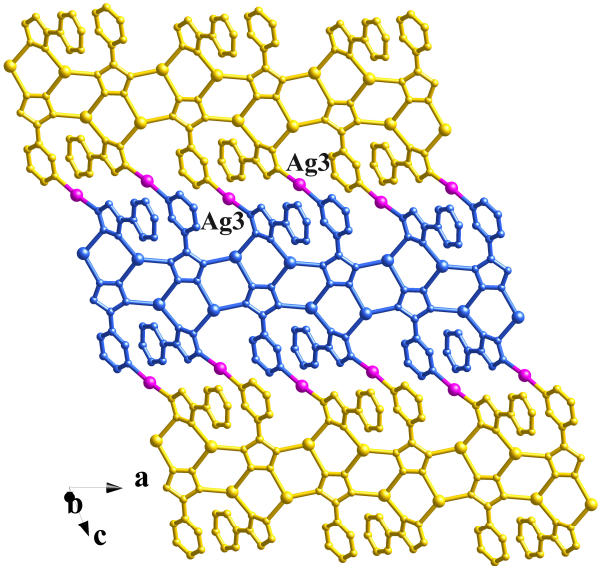

Fig. S4 The neighboring 1D belts connecting with each other to form a 2D network in **2** by the linkages of Ag3 atoms.

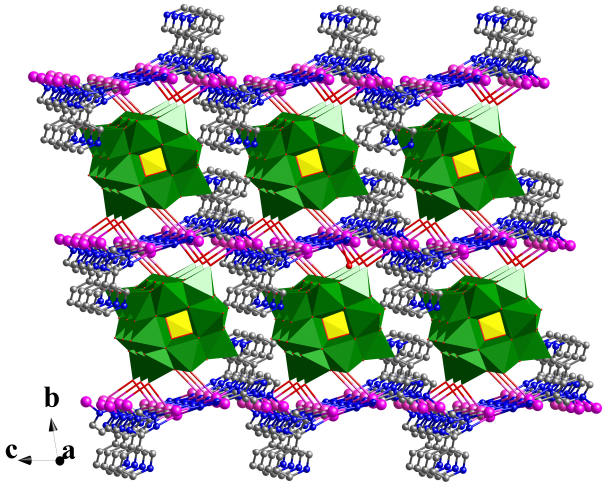

Fig. S5 The 3D framework of **2**.

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

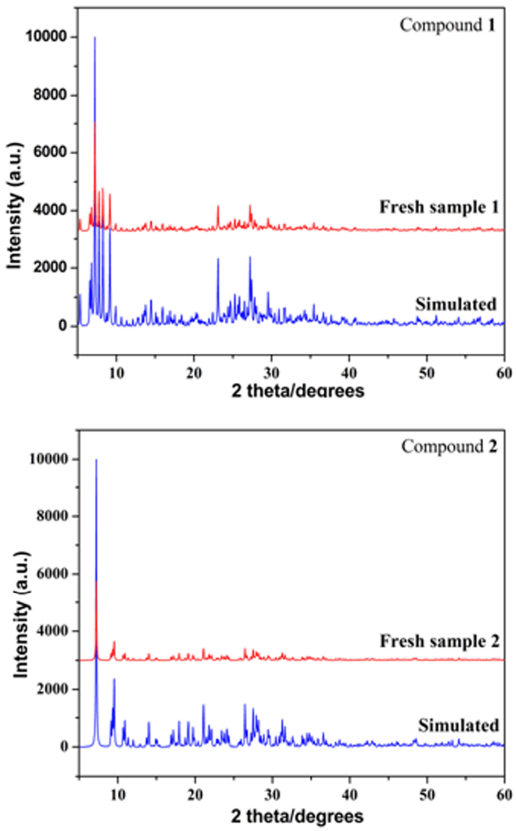

Fig. S6 The PXRD patterns of compounds **1** and **2**.

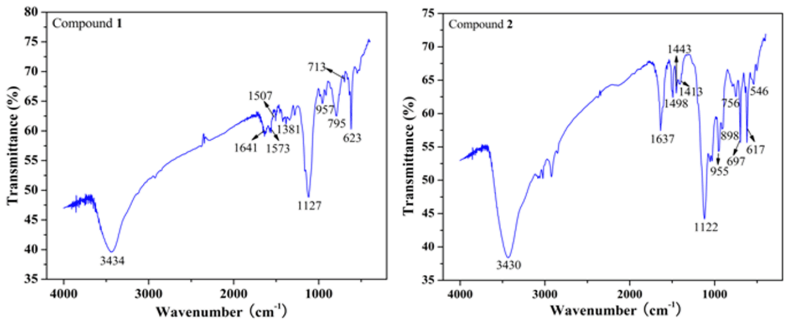

Fig. S7 The IR spectra of compounds **1** and **2**.

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

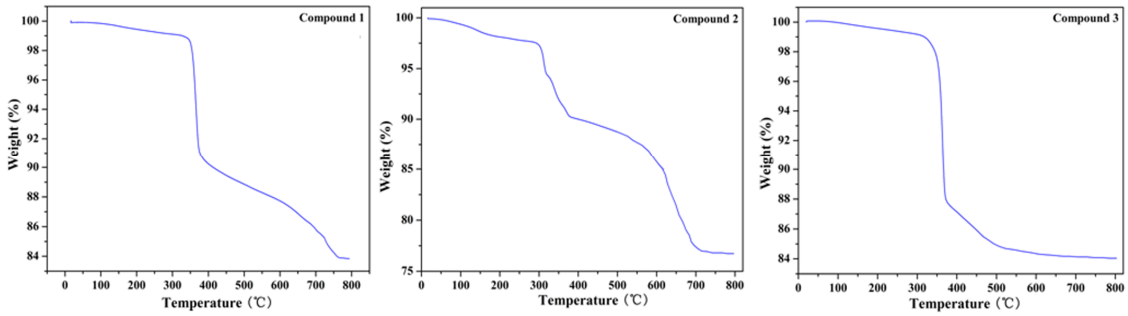

Fig. S8 The TG curves of compounds **1–3**.

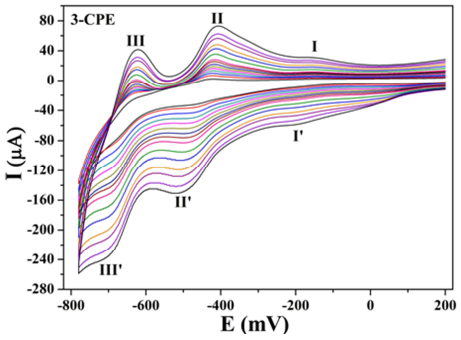

Fig. S9 The cyclic voltammograms of the **3**–CPE in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160, 180, 200, 250, 300, 350, 400, 450 and 500 $mV \cdot s^{-1}$, respectively).

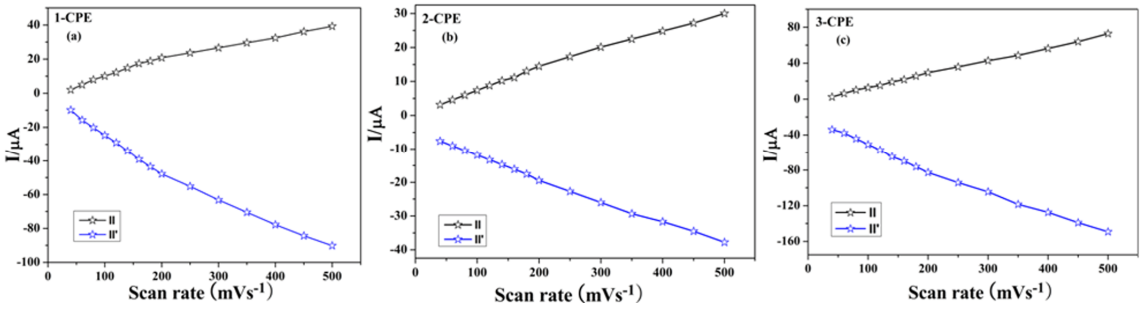

Fig. S10 The dependence of anodic peak (II) and cathodic peak (II') currents of **1**– (a), **2**– (b) and **3**–CPEs (c) on scan rates.

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

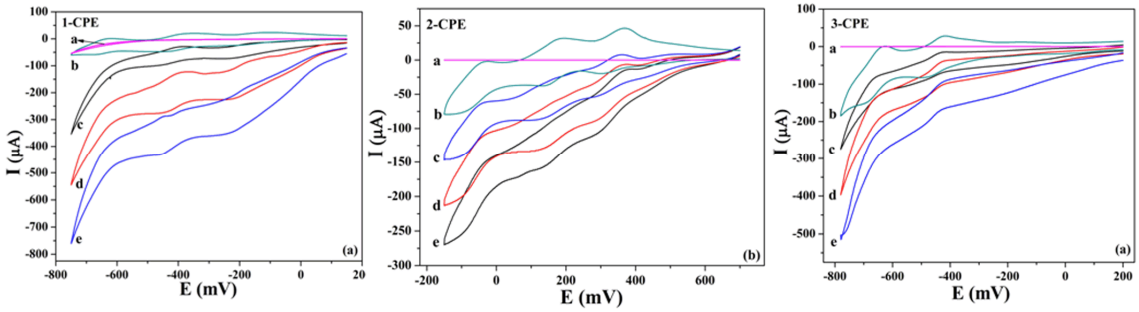

Fig. S11 Cyclic voltammograms of the **1**– (a), **2**– (b) and **3**–CPEs (c) in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution containing 0(b); 2(c); 4(d) and 6(e) mM $NaNO_2$ and a bare CPE in a 4.0 mM $NaNO_2$ + 0.1M H_2SO_4 + 0.5M Na_2SO_4 solution. Scan rate: 200 $mV{\cdot}s^{-1}$.

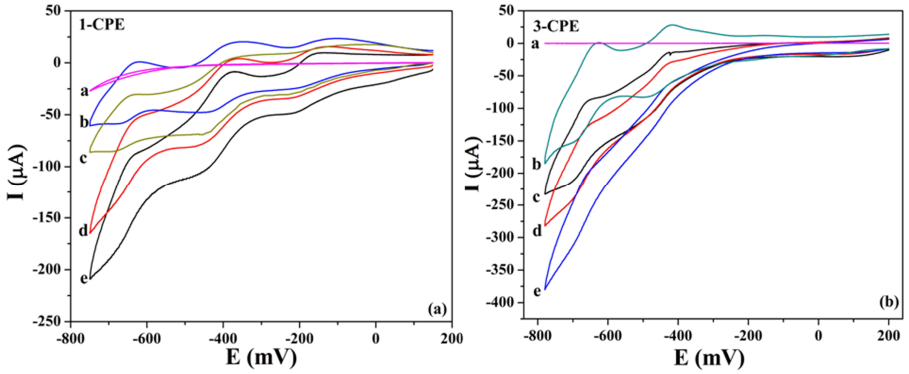

Fig. S12 Cyclic voltammograms of the **1**– (a) and **3**–CPEs (b) in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution containing 0(b); 2(c); 4(d) and 6(e) mM H_2O_2 and a bare CPE in a 4.0 mM H_2O_2 + 0.1M H_2SO_4 + 0.5M Na_2SO_4 solution. Scan rate: 200 $mV{\cdot}s^{-1}$.

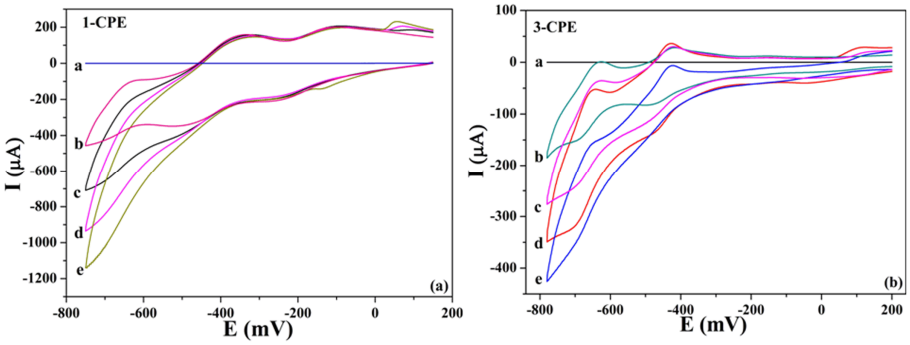

Fig. S13 Cyclic voltammograms of the **1**– (a) and **3**–CPEs (b) in 0.1M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution containing 0(b); 2(c); 4(d) and 6(e) mM $KBrO_3$ and a bare CPE in a 4.0 mM $KBrO_3$ + 0.1M H_2SO_4 + 0.5M Na_2SO_4 solution. Scan rate: 200 $mV{\cdot}s^{-1}$.

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

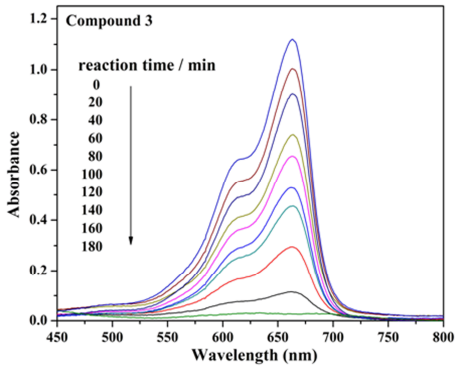

Fig. S14 Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of compound **3**.

Table S1. Selected bond distances (Å) and angles (°) for compounds **1** and **2**.

Compound **1**

Ag(1)-N(1)	2.181(15)	Ag(1)-N(6)	2.192(15)
Ag(2)-N(19)#1	2.184(15)	Ag(2)-O(49)	2.289(12)
Ag(2)-N(17)	2.292(15)	N(19)-Ag(2)#1	2.184(15)
Ag(3)-N(3)	2.190(14)	Ag(3)-N(11)	2.176(15)
N(14)-Ag(4)#6	2.190(14)	Ag(4)-N(14)#3	2.190(14)
Ag(4)-N(16)	2.204(16)	Ag(4)-O(51)	2.542(12)
N(2)-Ag(5)#2	2.128(16)	Ag(5)-N(2)#4	2.128(16)
Ag(5)-N(5)	2.154(15)	Ag(6)-N(15)#5	2.155(15)
Ag(6)-N(20)	2.174(17)	O(1W)-Ag(6)	2.520(15)
N(15)-Ag(6)#5	2.155(15)	N(18)-Ag(7)#1	2.390(14)
Ag(7)-N(13)	2.211(16)	Ag(7)-O(63)	2.33(2)
Ag(7)-N(18)#1	2.390(14)	N(1)-Ag(1)-N(6)	168.3(6)
C(24)-N(1)-Ag(1)	136.4(13)	N(16)-N(1)-Ag(1)	117.1(10)
N(12)-N(6)-Ag(1)	117.2(12)	N(5)-N(6)-Ag(1)	126.0(12)
N(16)-N(19)-Ag(2)#1	132.4(11)	N(18)-N(19)-Ag(2)#1	115.5(10)
W(3)-O(49)-Ag(2)	139.0(6)	O(49)-Ag(2)-N(17)	98.7(5)
N(13)-N(17)-Ag(2)	115.0(12)	N(14)-N(17)-Ag(2)	133.0(11)

N(19)#1-Ag(2)-O(49)	134.0(5)	N(19)#1-Ag(2)-N(17)	127.1(5)
N(11)-Ag(3)-N(3)	150.5(6)	N(20)-N(11)-Ag(3)	122.3(11)
N(13)-N(3)-Ag(3)	114.9(10)	C(2)-N(3)-Ag(3)	140.4(13)
C(15)-N(11)-Ag(3)	131.3(12)	N(16)-Ag(4)-O(51)	91.7(5)
N(14)#3-Ag(4)-N(16)	158.7(6)	N(14)#3-Ag(4)-O(51)	109.3(5)
C(2)-N(14)-Ag(4)#6	132.9(12)	N(17)-N(14)-Ag(4)#6	120.5(10)
N(19)-N(16)-Ag(4)	121.8(11)	N(1)-N(16)-Ag(4)	129.5(12)
W(17)-O(51)-Ag(4)	138.8(6)	C(15)-N(2)-Ag(5)#2	134.3(14)
N(10)-N(2)-Ag(5)#2	117.3(11)	N(2)#4-Ag(5)-N(5)	169.8(6)
N(6)-N(5)-Ag(5)	130.8(11)	N(15)-N(5)-Ag(5)	120.5(12)
C(1)-N(15)-Ag(6)#5	131.7(11)	N(5)-N(15)-Ag(6)#5	123.1(11)
N(10)-N(20)-Ag(6)	116.6(12)	N(11)-N(20)-Ag(6)	128.6(12)
N(15)#5-Ag(6)-N(20)	170.6(6)	N(15)#5-Ag(6)-O(1W)	91.1(5)
N(20)-Ag(6)-O(1W)	96.4(5)	N(13)-Ag(7)-O(63)	132.0(6)
N(13)-Ag(7)-N(18)#1	121.1(5)	O(63)-Ag(7)-N(18)#1	101.7(6)
N(17)-N(13)-Ag(7)	121.3(12)	N(3)-N(13)-Ag(7)	131.1(11)
C(24)-N(18)-Ag(7)#1	128.8(12)	N(19)-N(18)-Ag(7)#1	116.4(10)

Symmetry codes for **1**: #1 -x+2, -y+1, -z+2 #2 x-1, y, z+1 #3 x+1, y, z

#4 x+1, y, z-1 #5 -x+2, -y, -z+2 #6 x-1, y, z

Compound **2**

Ag(1)-N(10)#1	2.203(10)	Ag(1)-N(6)	2.227(11)
N(10)-Ag(1)#1	2.203(10)	Ag(1)-N(9)	2.294(9)
N(3)-Ag(2)#2	2.198(10)	Ag(2)-N(3)#2	2.198(11)
Ag(2)-N(1)	2.265(10)	Ag(2)-N(5)	2.245(10)
Ag(3)-N(2)#3	2.118(11)	N(2)-Ag(3)#4	2.118(11)
Ag(3)-N(7)	2.157(10)	N(10)#1-Ag(1)-N(6)	140.1(4)
N(1)-N(9)-Ag(1)	117.5(7)	N(10)#1-Ag(1)-N(9)	106.6(4)
N(9)-N(10)-Ag(1)#1	120.5(7)	N(6)-Ag(1)-N(9)	111.9(4)
N(2)-N(6)-Ag(1)	125.2(8)	N(10)-N(9)-Ag(1)	131.6(7)

Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry

N(5)-N(6)-Ag(1)	118.9(8)	C(5)-N(10)-Ag(1)#1	132.3(8)
N(5)-Ag(2)-N(1)	110.2(4)	N(3)#2-Ag(2)-N(5)	131.2(4)
N(6)-N(5)-Ag(2)	111.2(8)	C(5)-N(3)-Ag(2)#2	137.1(8)
N(9)-N(1)-Ag(2)	127.4(7)	N(3)#2-Ag(2)-N(1)	118.5(4)
N(3)-N(1)-Ag(2)	124.7(7)	N(1)-N(3)-Ag(2)#2	115.5(7)
C(6)-N(5)-Ag(2)	136.9(8)	N(6)-N(2)-Ag(3)#4	122.8(8)
N(2)#3-Ag(3)-N(7)	172.5(4)	C(7)-N(7)-Ag(3)	118.0(9)
N(4)-N(2)-Ag(3)#4	127.1(8)	C(10)-N(7)-Ag(3)	123.4(9)

Symmetry codes for **2**: #1 -x+2, -y+2, -z #2 -x+1, -y+2, -z #3 x, y, z-1 #4 x, y, z+1 #5 -x+2, -y+1, -z