Supporting Information

Syntheses, structures and properties of two new organic-inorganic materials based on ε-Zn Keggin units {ε-$PMo^{V}_{8}Mo^{VI}_{4}O_{40-x}(OH)_{x}Zn_{4}$}

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Table S1 Mo-O and Mo-Mo distances (Å) and Bond Valence Sum Calculations

$\varepsilon(pyim)_2$			$\varepsilon_2(pyim)_6$		
	Mo1			Mo1	
Mo(1)-O(25)	1.690(7)		Mo(1)-O(36)	1.661(7)	
Mo(1)-O(1)	1.938(7)		Mo(1)-O(1)	1.973(6)	
Mo(1)-O(5)	1.956(7)		Mo(1)-O(9)	1.980(6)	
Mo(1)-O(36)	2.003(7)		Mo(1)-O(26)	1.998(6)	
Mo(1)-O(35)	2.076(7)		Mo(1)-O(3)	2.033(6)	
Mo(1)-O(19)	2.436(6)		Mo(1)-Mo(2)	2.6157(11)	Σ = 4.87
Mo(1)-Mo(2)	2.5781(13)	Σ = 4.91		Mo2	
	Mo2		Mo(2)-O(31)	1.653(7)	
Mo(2)-O(21)	1.682(7)		Mo(2)-O(1)	1.944(6)	
Mo(2)-O(5)	1.954(7)		Mo(2)-O(9)	1.966(6)	
Mo(2)-O(1)	1.959(7)		Mo(2)-O(24)	2.032(6)	
Mo(2)-O(34)	1.981(7)		Mo(2)-O(25)	2.084(6)	Σ = 4.77
Mo(2)-O(14)	2.089(7)			Mo3	
Mo(2)-O(15)	2.511(6)	Σ = 4.80	Mo(3)-O(28)	1.683(6)	
	Mo3		Mo(3)-O(23)	1.817(6)	
Mo(3)-O(32)	1.693(7)		Mo(3)-O(24)	1.833(6)	

Mo(3)-O(36)	1.823(7)		Mo(3)-O(12)	1.980(6)	
Mo(3)-O(31)	1.840(7)		Mo(3)-O(5)	2.030(6)	
Mo(3)-O(29)	1.988(6)		Mo(3)-Mo(7)	3.1662(12)	Σ = 5.63
Mo(3)-O(8)	2.000(6)			Mo4	
Mo(3)-Mo(5)	3.1627(13)	Σ = 5.56	Mo(4)-O(17)	1.682(6)	
	Mo4		Mo(4)-O(2)	1.937(6)	
Mo(4)-O(26)	1.675(7)		Mo(4)-O(7)	1.962(6)	
Mo(4)-O(2)	1.950(6)		Mo(4)-O(35)	2.018(6)	
Mo(4)-O(10)	1.971(7)		Mo(4)-O(29)	2.070(7)	
Mo(4)-O(31)	2.019(7)		Mo(4)-Mo(9)	2.6159(12)	Σ = 4.75
Mo(4)-O(35)	2.079(7)			Mo5	
Mo(4)-O(19)	2.518(6)		Mo(5)-O(34)	1.684(6)	
Mo(4)-Mo(6)	2.5949(13)	Σ = 4.85	Mo(5)-O(30)	1.818(6)	
	Mo5		Mo(5)-O(26)	1.819(6)	
Mo(5)-O(28)	1.684(7)		Mo(5)-O(15)	1.992(6)	
Mo(5)-O(22)	1.805(7)		Mo(5)-O(21)	2.027(7)	
Mo(5)-O(37)	1.820(6)		Mo(5)-Mo(10)	3.1373(13)	Σ = 5.66
Mo(5)-O(29)	2.000(6)			Mo6	
Mo(5)-O(8)	2.021(6)	Σ = 5.68	Mo(6)-O(27)	1.681(6)	
	Mo6		Mo(6)-O(8)	1.944(6)	
Mo(6)-O(23)	1.665(7)		Mo(6)-O(4)	1.965(6)	
Mo(6)-O(2)	1.956(7)		Mo(6)-O(33)	1.999(6)	
Mo(6)-O(10)	1.978(7)		Mo(6)-O(32)	2.080(7)	
Mo(6)-O(3)#1	2.011(6)		Mo(6)-O(10)	2.448(6)	
Mo(6)-O(17)	2.022(7)		Mo(6)-Mo(8)	2.5840(12)	Σ = 4.92
Mo(6)-O(13)	2.499(6)	Σ = 4.92		Mo7	
	Mo7		Mo(7)-O(14)	1.695(6)	
Mo(7)-O(30)	1.666(7)		Mo(7)-O(37)	1.814(6)	
Mo(7)-O(11)	1.950(7)		Mo(7)-O(35)	1.831(6)	
Mo(7)-O(9)	1.960(6)		Mo(7)-O(12)	2.001(6)	
Mo(7)-O(16)#2	2.028(6)		Mo(7)-O(5)	2.025(6)	Σ = 5.52
Mo(7)-O(37)	2.032(7)			Mo8	
Mo(7)-Mo(11)	2.6229(13)	Σ = 4.88	Mo(8)-O(20)	1.685(6)	
	Mo8		Mo(8)-O(4)	1.953(6)	
Mo(8)-O(39)	1.685(7)		Mo(8)-O(8)	1.973(6)	
Mo(8)-O(17)	1.806(6)		Mo(8)-O(23)	2.015(6)	
Mo(8)-O(24)	1.836(7)		Mo(8)-O(25)	2.068(6)	
Mo(8)-O(27)	1.965(7)		Mo(8)-O(16)	2.470(6)	Σ = 4.73
Mo(8)-O(7)	2.022(6)			Mo9	
Mo(8)-Mo(10)	3.1387(13)	Σ = 5.70	Mo(9)-O(22)	1.674(6)	
	Mo9		Mo(9)-O(2)	1.970(6)	
Mo(9)-O(38)	1.672(7)		Mo(9)-O(7)	1.976(6)	
Mo(9)-O(4)	1.965(7)		Mo(9)-O(30)	2.012(6)	
Mo(9)-O(6)	1.966(7)		Mo(9)-O(3)	2.036(6)	Σ = 4.67

Mo(9)-O(16)#2	2.009(7)			Mo10	
Mo(9)-O(22)	2.027(7)		Mo(10)-O(19)	1.712(6)	
Mo(9)-O(12)	2.500(6)		Mo(10)-O(40)	1.845(7)	
Mo(9)-Mo(12)	2.5984(13)	Σ = 4.97	Mo(10)-O(33)	1.848(6)	
	Mo10		Mo(10)-O(15)	1.969(6)	
Mo(10)-O(40)	1.692(7)		Mo(10)-O(21)	1.978(6)	Σ = 5.42
Mo(10)-O(33)	1.819(7)			Mo11	
Mo(10)-O(34)	1.839(7)		Mo(11)-O(38)	1.669(7)	
Mo(10)-O(27)	1.969(7)		Mo(11)-O(18)	1.956(6)	
Mo(10)-O(7)	2.002(6)	Σ = 5.61	Mo(11)-O(6)	1.958(6)	
	Mo11		Mo(11)-O(37)	2.012(6)	
Mo(11)-O(18)	1.680(7)		Mo(11)-O(29)	2.075(6)	
Mo(11)-O(11)	1.965(6)		Mo(11)-O(11)	2.459(6)	
Mo(11)-O(9)	1.965(7)		Mo(11)-Mo(12)	2.5736(12)	Σ = 4.96
Mo(11)-O(24)	2.009(7)			Mo12	
Mo(11)-O(3)#1	2.014(6)	Σ = 4.72	Mo(12)-O(39)	1.677(7)	
	Mo12		Mo(12)-O(6)	1.945(6)	
Mo(12)-O(20)	1.664(7)		Mo(12)-O(18)	1.961(6)	
Mo(12)-O(4)	1.941(7)		Mo(12)-O(40)	1.996(6)	
Mo(12)-O(6)	1.961(7)		Mo(12)-O(32)	2.079(6)	
Mo(12)-O(33)	1.997(7)		Mo(12)-O(10)	2.475(6)	Σ = 4.85
Mo(12)-O(14)	2.085(7)				
Mo(12)-O(15)	2.514(6)	Σ = 4.91			

1. Table S2. Table S2. Hydrogen bonds for compounds **ε(pyim)$_2$** and **ε$_2$(pyim)$_6$** have been added in the supporting information.

ε(pyim)$_2$

D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°
N3-H3B···O37	0.86	2.01	2.781(14)	149
N3-H3B···O23	0.86	2.38	2.895(12)	119
N6-H6A···O39	0.86	2.25	2.929(13)	136
N6-H6A···O40	0.86	2.58	2.988(11)	110
C1-H1A···O35	0.93	2.46	3.277(19)	146
C8-H8A···O40	0.93	2.40	3.238(16)	149
C8-H8A···O40	0.93	2.57	3.133(15)	119
C9-H9A···O22	0.93	2.59	3.181(15)	122
C9-H9A···O38	0.93	2.52	3.415(15)	163
C12-H12A···O39	0.93	2.54	3.185(15)	126
C15-H15A···O25	0.93	2.58	3.476(15)	163

ε$_2$(pyim)$_6$

D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	∠D-H-A/°

N2A-H2AB···O24	0.86	2.04	2.890(8)	170
N4A-H4AA···O43	0.86	1.85	2.701(9)	173
C1-H1A···O2	0.93	2.55	2.952(10)	106
C1-H1A···O55	0.93	2.58	3.247(12)	129
C3A-H3AA···O31	0.93	2.32	3.204(10)	159
C5-H5A···O24	0.93	2.40	3.280(11)	157
C6A-H6AA···O17	0.93	2.54	3.205(11)	129
C6A-H6AA···O48	0.93	2.47	3.186(11)	134
C9-H9A···O19	0.93	2.57	3.272(11)	133
C10-H10A···O46	0.93	2.48	3.322(12)	150
C11-H11A···O6	0.93	2.47	3.011(12)	117
C13-H13A···O50	0.93	2.39	3.176(14)	141
C14-H14A···O2W	0.93	2.23	3.121(19)	161
C21-H21A···O24	0.93	2.36	3.256(10)	161
C25-H25A···O9	0.93	2.46	2.880(10)	108
C26-H26A···O34	0.93	2.35	2.913(12)	118
C29-H29A···O50	0.93	2.52	3.086(10)	119
C30-H30A···O37	0.93	2.58	2.984(11)	106
C30-H30A···O47	0.93	2.43	3.278(12)	151
C32-H32A···O32	0.93	2.39	3.136(11)	137
C32-H32A···O61	0.93	2.48	3.266(12)	142
C35-H35A···O1	0.93	2.59	2.932(18)	102
C35A-H35B···O13	0.93	2.46	3.051(11)	121
C37-H37A···O8	0.93	2.20	3.02(2)	146.
C37-H37A···O58	0.93	2.50	3.135(19)	126.
C39-H39A···O26	0.96	2.30	3.244(16)	170

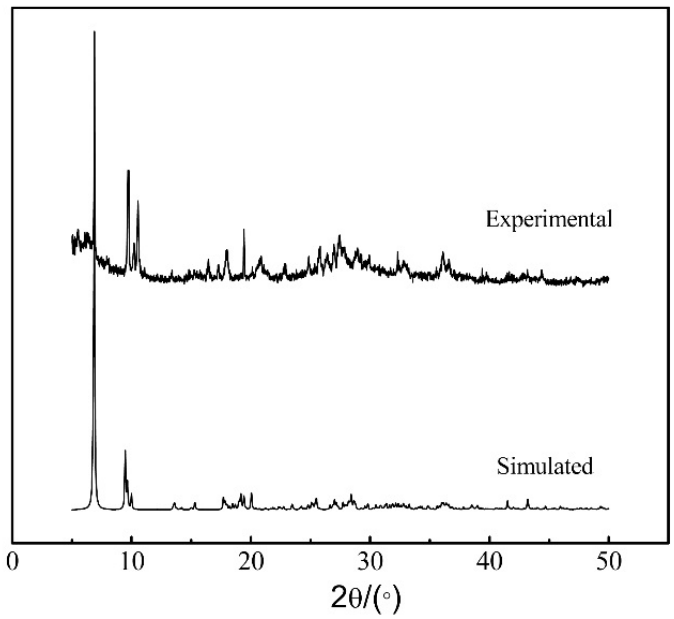

Fig. S1 Experimental and simulated power XRD patterns of **ε(pyim)$_2$**.

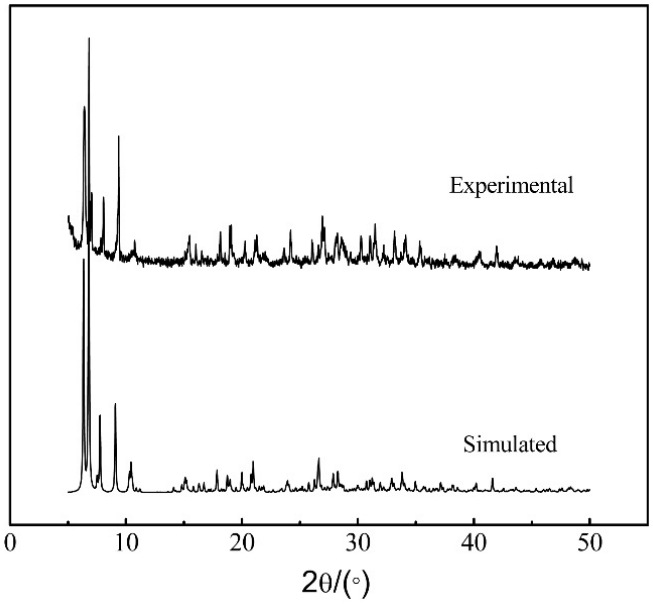

Fig. S2 Experimental and simulated power XRD patterns of **ε_2(pyim)$_6$**.

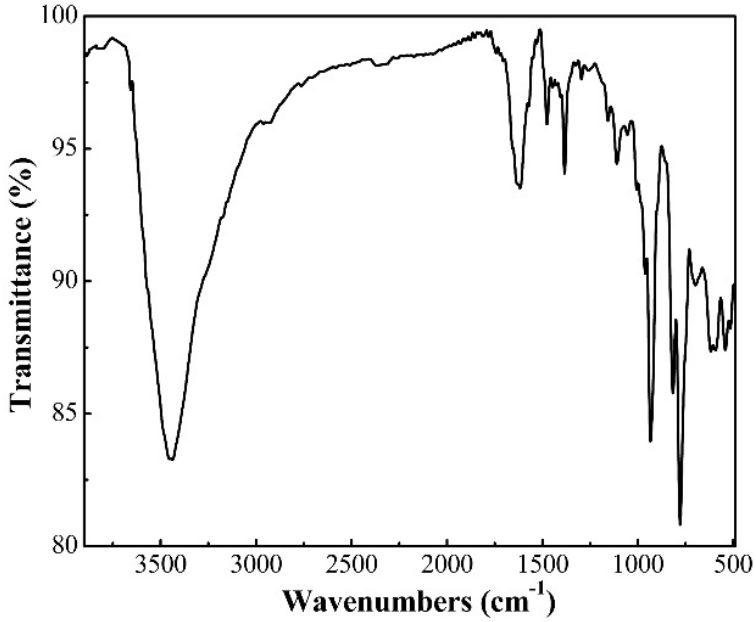

Fig. S3 IR spectra of **ε(pyim)$_2$**.

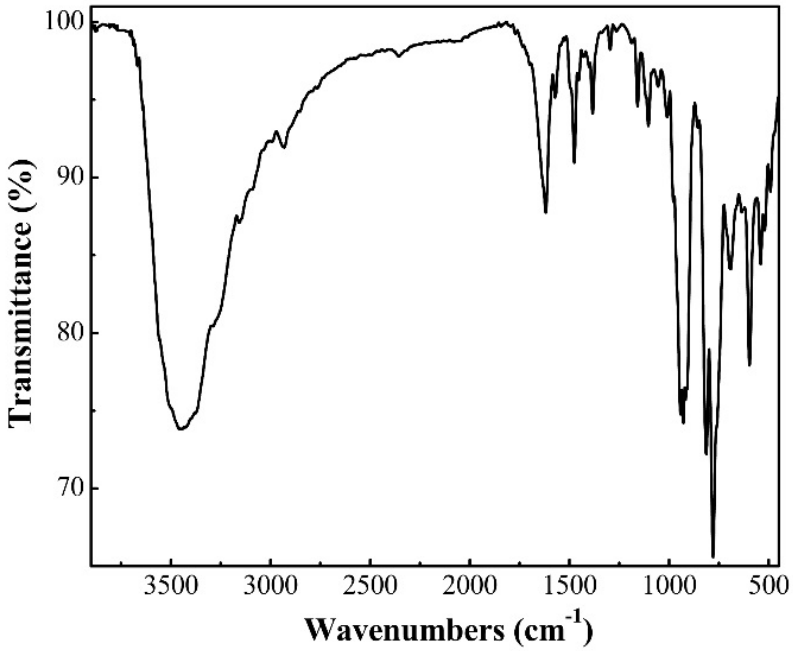

Fig. S4 IR spectra of $\varepsilon_2(pyim)_6$.

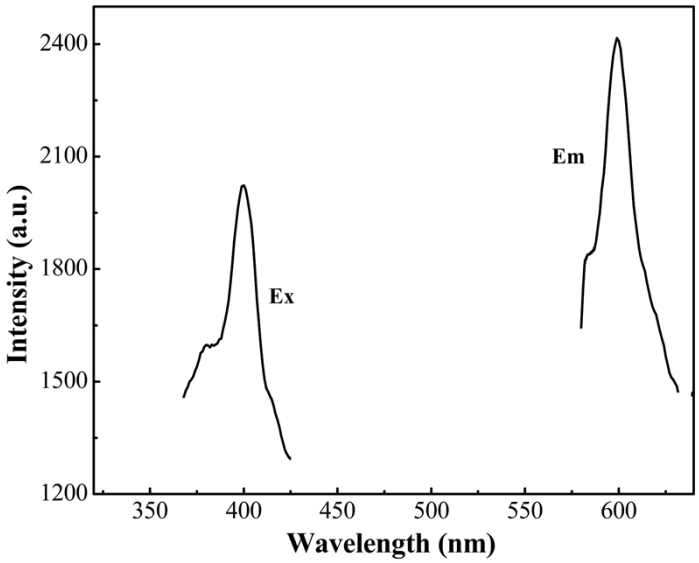

Fig. S5 The excitation and emission spectrum of $\varepsilon(pyim)_2$ at room temperature.

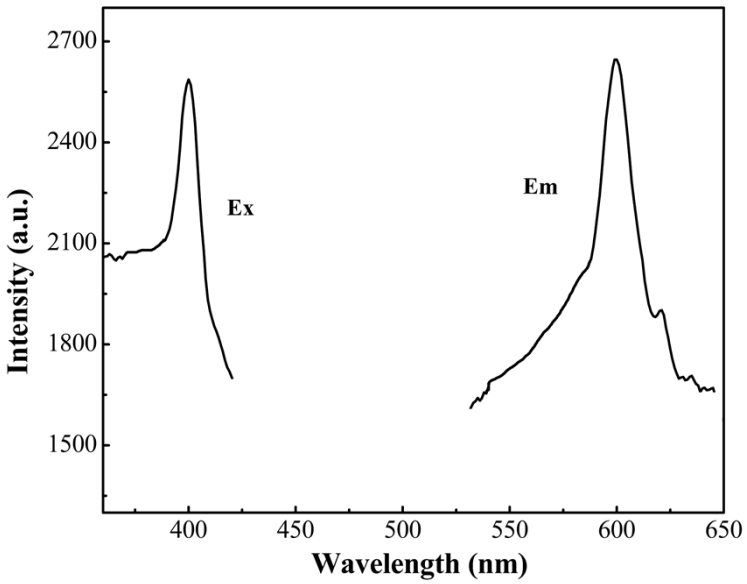

Fig. S6 The excitation and emission spectrum of $\boldsymbol{\varepsilon_2(pyim)_6}$ at room temperature.

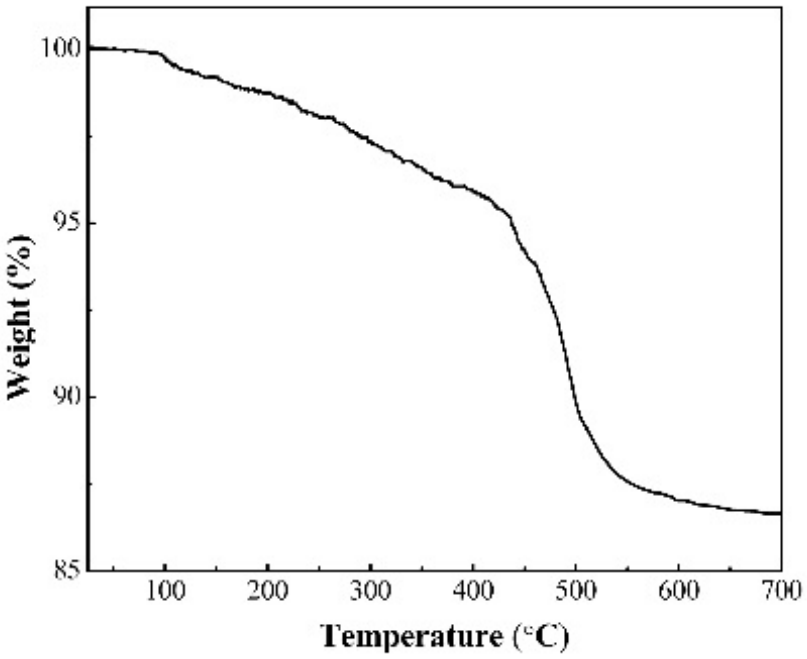

Fig. S7 TG curves of $\boldsymbol{\varepsilon(pyim)_2}$.

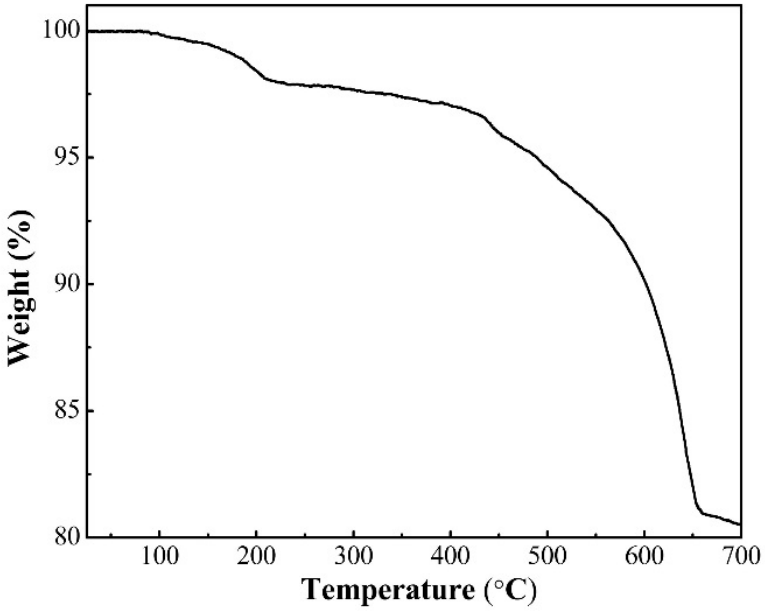

Fig. S8 TG curves of **ε_2(pyim)$_6$.**