

## Electronic Supplementary Information (ESI)

### **POM-based inorganic-organic hybrid compounds: synthesis, structures, high-connected topologies and photodegradation of Organic dyes**

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**Table S1. Selected Bonds Lengths (Å) and Angles (°) for compounds 1-4**

Compound 1			
Mn(1)-O(1A)	1.995(2)	O(1A) -Mn(1)-N(2)	90.36(11)
Mn(1)-O(1)	1.995(2)	O(1)-Mn(1)-N(2)	89.64(11)
Mn(1)-N(2A)	2.189(3)	N(2A) -Mn(1)-N(2)	180.0
Mn(1)-N(2)	2.189(3)	O(1A) -Mn(1)-N(1A)	90.31(11)
Mn(1)-N(1A)	2.224(3)	O(1)-Mn(1)-N(1A)	89.69(11)
Mn(1)-N(1)	2.224(3)	N(2A) -Mn(1)-N(1A)	89.47(12)
V(1)-O(2)	1.615(3)	N(2)-Mn(1)-N(1A)	90.53(12)
V(1)-O(1)	1.651(2)	O(1A) -Mn(1)-N(1)	89.69(11)
V(1)-O(3)	1.771(3)	O(1)-Mn(1)-N(1)	90.31(11)
O(1A) -Mn(1)-O(1)	180.00(14)	N(2A) -Mn(1)-N(1)	90.53(12)
O(1A) -Mn(1)-N(2A)	89.64(11)	N(2)-Mn(1)-N(1)	89.47(12)
O(1)-Mn(1)-N(2A)	90.36(11)	N(1A) -Mn(1)-N(1)	180.0
O(2)-V(1)-O(1)	108.99(16)	V(1)-O(1)-Mn(1)	177.64(18)
O(2)-V(1)-O(3)	110.49(19)	V(1)-O(3)-V(1C)	155.1(2)
Compound 2			
Ag(1)-N(4)	2.212(8)	O(1)-V(1)-O(2)	109.3(4)
Ag(1)-N(3)	2.222(8)	O(1)-V(1)-O(3)	111.2(4)
Ag(2)-N(2)	2.121(8)	O(2)-V(1)-O(3)	111.3(4)
Ag(2)-N(1)	2.145(9)	O(1)-V(1)-O(4)	109.5(4)
Ag(2)-O(6)	2.374(8)	O(2)-V(1)-O(4)	105.7(4)
V(1)-O(1)	1.607(7)	O(3)-V(1)-O(4)	109.8(3)
V(1)-O(2)	1.608(7)	O(5)-V(2)-O(6)	109.6(4)
V(1)-O(3)	1.785(7)	O(5)-V(2)-O(3)#3	109.5(4)
V(1)-O(4)	1.807(8)	O(6)-V(2)-O(3)#3	109.3(4)
O(6)-V(2)-O(4)	106.6(4)	O(5)-V(2)-O(4)	110.7(4)
V(2)-O(5)	1.594(8)	O(3)#3-V(2)-O(4)	111.0(3)
V(2)-O(6)	1.606(8)	V(2)#3-O(3)-V(1)	155.9(5)
V(2)-O(3)#3	1.775(7)	V(1)-O(4)-V(2)	132.1(5)

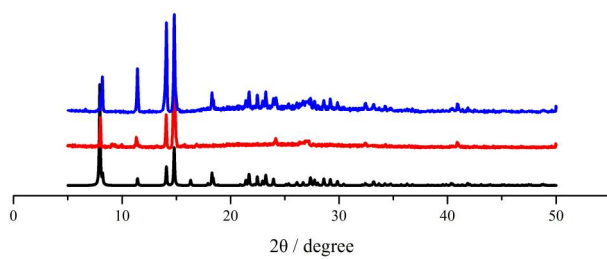
V(2)-O(4)	1.814(7)	V(2)-O(6)-Ag(2)	153.8(5)
O(3)-V(2)#3	1.775(7)	N(2)-Ag(2)-O(6)	104.7(3)
N(4)-Ag(1)-N(3)	160.7(3)	N(1)-Ag(2)-O(6)	95.8(3)
N(2)-Ag(2)-N(1)	158.1(3)		
Compound 3			
Ni(1)-O(4)	2.042(2)	Ni(1)-O(1W)	2.113(3)
Ni(1)-N(4)	2.077(2)	Ni(2)-N(2B)	2.102(2)
Ni(1)-N(3)	2.083(2)	Ni(2)-N(2)	2.102(2)
Ni(1)-O(8)	2.085(2)	Ni(2)-O(1B)	2.111(2)
Ni(1)-O(2W)	2.102(2)	Ni(2)-O(1)	2.111(2)
Ni(2)-N(1B)	2.158(2)	O(4)-Ni(1)-N(4)	93.71(9)
Ni(2)-N(1)	2.158(2)	O(4)-Ni(1)-N(3)	94.42(9)
V(1)-O(7)	1.620(2)	N(4)-Ni(1)-N(3)	88.12(9)
V(1)-O(8)	1.659(2)	O(4)-Ni(1)-O(8)	170.66(8)
V(1)-O(9)	1.771(2)	N(4)-Ni(1)-O(8)	93.97(9)
V(1)-O(6)	1.809(2)	N(3)-Ni(1)-O(8)	91.14(9)
V(2)-O(5)	1.614(2)	O(4)-Ni(1)-O(2W)	87.70(9)
V(2)-O(4D)	1.650(2)	N(4)-Ni(1)-O(2W)	86.17(9)
V(2)-O(9E)	1.792(2)	N(3)-Ni(1)-O(2W)	174.03(9)
V(2)-O(2)	1.8059(19)	O(8)-Ni(1)-O(2W)	87.52(9)
V(3)-O(3)	1.650(2)	O(4)-Ni(1)-O(1W)	84.98(10)
V(3)-O(1)	1.651(2)	N(4)-Ni(1)-O(1W)	175.00(10)
V(3)-O(2)	1.7786(19)	N(3)-Ni(1)-O(1W)	96.79(10)
V(3)-O(6)	1.779(2)	O(8)-Ni(1)-O(1W)	86.92(10)
O(4)-V(2D)	1.650(2)	O(2W)-Ni(1)-O(1W)	88.96(10)
O(9)-V(2)#4	1.792(2)	N(2B) -Ni(2)-N(2)	180.0
O(1B) -Ni(2)-N(1)	90.05(8)	N(2B) -Ni(2)-O(1B)	90.46(8)
O(1)-Ni(2)-N(1)	89.95(8)	N(2)-Ni(2)-O(1B)	89.54(8)
N(1B) -Ni(2)-N(1)	180.0	O(4)-Ni(1)-O(1W)	84.98(10)
O(7)-V(1)-O(8)	106.97(11)	N(4)-Ni(1)-O(1W)	175.00(10)
O(7)-V(1)-O(9)	108.21(13)	N(2B) -Ni(2)-O(1)	89.54(8)

O(8)-V(1)-O(9)	112.68(12)	N(2)-Ni(2)-O(1)	90.46(8)
O(7)-V(1)-O(6)	110.40(12)	O(1B) -Ni(2)-O(1)	180.0
O(8)-V(1)-O(6)	109.76(10)	N(2B) -Ni(2)-N(1B)	86.55(8)
O(9)-V(1)-O(6)	108.80(11)	N(2)-Ni(2)-N(1B)	93.45(8)
O(5)-V(2)-O(4D)	109.05(13)	O(1B) -Ni(2)-N(1B)	89.95(8)
O(5)-V(2)-O(9E)	108.97(14)	O(1)-Ni(2)-N(1B)	90.05(8)
O(4D) -V(2)-O(9E)	109.84(11)	N(2B)-Ni(2)-N(1)	93.45(8)
O(5)-V(2)-O(2)	109.10(12)	N(2)-Ni(2)-N(1)	86.55(8)
O(4D) -V(2)-O(2)	109.44(10)	N(2B) -Ni(2)-O(1)	89.54(8)
O(9E) -V(2)-O(2)	110.41(11)	V(3)-O(2)-V(2)	140.90(12)
O(3)-V(3)-O(1)	110.09(10)	V(2D) -O(4)-Ni(1)	167.78(13)
O(3)-V(3)-O(2)	109.42(10)	V(3)-O(6)-V(1)	133.26(12)
O(1)-V(3)-O(2)	109.41(10)	V(1)-O(9)-V(2)#4	153.98(18)
O(3)-V(3)-O(6)	107.82(10)	V(1)-O(8)-Ni(1)	142.01(12)
O(1)-V(3)-O(6)	108.56(10)	V(3)-O(1)-Ni(2)	168.40(12)
O(2)-V(3)-O(6)	111.53(10)		
Compound 4			
V(1)-O(8)	1.624(4)	V(2)-O(5)	1.663(3)
V(1)-O(1)	1.656(3)	V(2)-O(6)	1.780(3)
V(1)-O(3)	1.777(3)	V(2)-O(10)#1	1.785(3)
V(1)-O(10)	1.809(3)	Zn(1)-O(5)#2	2.126(3)
V(2)-O(4)	1.647(3)	Zn(1)-O(5)	2.126(3)
Zn(1)-N(2)#2	2.148(3)	O(8)-V(1)-O(1)	107.06(18)
Zn(1)-N(2)	2.148(3)	O(8)-V(1)-O(3)	108.6(2)
Zn(1)-N(3)	2.207(3)	O(1)-V(1)-O(3)	112.28(18)
Zn(1)-N(3)#2	2.207(3)	O(8)-V(1)-O(10)	109.96(19)
Zn(2)-O(2)	2.068(3)	O(1)-V(1)-O(10)	109.96(16)
Zn(2)-N(4)	2.130(4)	O(3)-V(1)-O(10)	108.91(16)
Zn(2)-N(1)	2.131(4)	O(4)-V(2)-O(5)	109.71(16)
Zn(2)-O(1)	2.137(3)	O(4)-V(2)-O(6)	109.63(15)
Zn(2)-O(1W)	2.141(3)	O(5)-V(2)-O(6)	109.20(15)

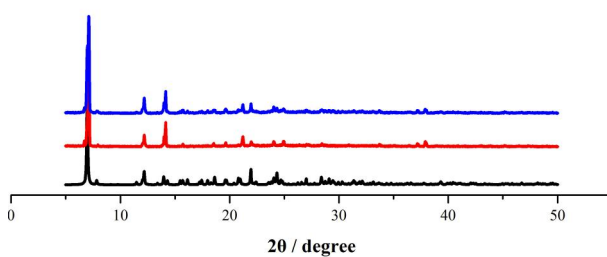
Zn(2)-O(2W)	2.169(3)	O(4)-V(2)-O(10)#1	107.95(15)
V(3)-O(7)	1.611(4)	O(5)-V(2)-O(10)#1	108.64(15)
V(3)-O(2)	1.648(3)	O(6)-V(2)-O(10)#1	111.68(16)
V(3)-O(3)#3	1.789(4)	O(5)#2-Zn(1)-O(5)	180.00(13)
V(3)-O(6)	1.809(3)	O(5)#2-Zn(1)-N(2)#2	90.59(12)
O(3)-V(3)#8	1.789(4)	O(5)-Zn(1)-N(2)#2	89.41(12)
O(10)-V(2)#1	1.785(3)	O(5)#2-Zn(1)-N(2)	89.41(12)
N(2)#2-Zn(1)-N(3)	94.06(13)	O(5)-Zn(1)-N(2)	90.59(12)
N(2)-Zn(1)-N(3)	85.94(13)	N(2)#2-Zn(1)-N(2)	180.0(2)
O(5)#2-Zn(1)-N(3)#2	89.43(12)	O(5)#2-Zn(1)-N(3)	90.57(12)
O(5)-Zn(1)-N(3)#2	90.57(12)	O(5)-Zn(1)-N(3)	89.43(12)
N(2)#2-Zn(1)-N(3)#2	85.94(13)	N(2)#2-Zn(1)-N(3)	94.06(13)
N(2)-Zn(1)-N(3)#2	94.06(13)	N(2)-Zn(1)-N(3)	85.94(13)
N(3)-Zn(1)-N(3)#2	180.00(19)	O(5)#2-Zn(1)-N(3)#2	89.43(12)
O(2)-Zn(2)-N(4)	95.04(14)	O(5)-Zn(1)-N(3)#2	90.57(12)
O(2)-Zn(2)-N(1)	93.69(14)	N(2)#2-Zn(1)-N(3)#2	85.94(13)
N(4)-Zn(2)-N(1)	87.77(14)	N(2)-Zn(1)-N(3)#2	94.06(13)
O(7)-V(3)-O(2)	109.1(2)	N(3)-Zn(1)-N(3)#2	180.00(19)
O(7)-V(3)-O(3)#3	108.8(2)	O(2)-Zn(2)-N(4)	95.04(14)
O(2)-V(3)-O(3)#3	109.71(17)	O(2)-Zn(2)-N(1)	93.69(14)
O(7)-V(3)-O(6)	108.78(19)	N(4)-Zn(2)-N(1)	87.77(14)
O(2)-V(3)-O(6)	109.45(15)	O(1)-Zn(2)-O(2W)	87.22(12)
O(3)#3-V(3)-O(6)	111.00(16)	O(1W)-Zn(2)-O(2W)	87.19(13)

Symmetry codes: for compound **1**: (A)  $-x + 1, -y + 2, -z$ ; (C)  $x + 1/4, -y + 5/4, -z + 1/4$ ; for compound **2**: #3  $-x - 1, -y + 1, -z + 1$ ; for compound **3**: (B)  $-x, -y + 1, -z + 1$ ; (D)  $-x + 1, -y + 1, -z + 1$ ; (E)  $-x + 1/2, y + 1/2, -z + 1/2$ ; #4  $-x + 1/2, y - 1/2, -z + 1/2$ ; for compound **4**: #1  $-x - 1, -y, -z$ ; #2  $-x, -y, -z$ ; #3  $x + 1/2, -y - 1/2, z + 1/2$ ; #8  $x - 1/2, -y - 1/2, z - 1/2$ .

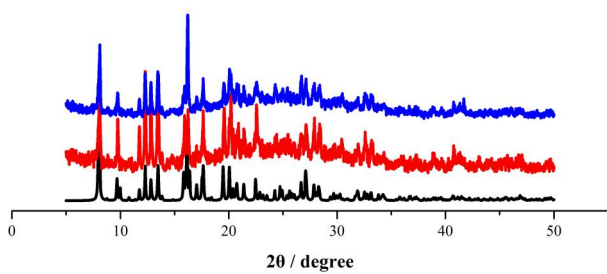
(a)



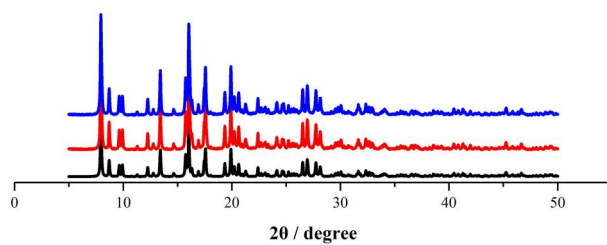
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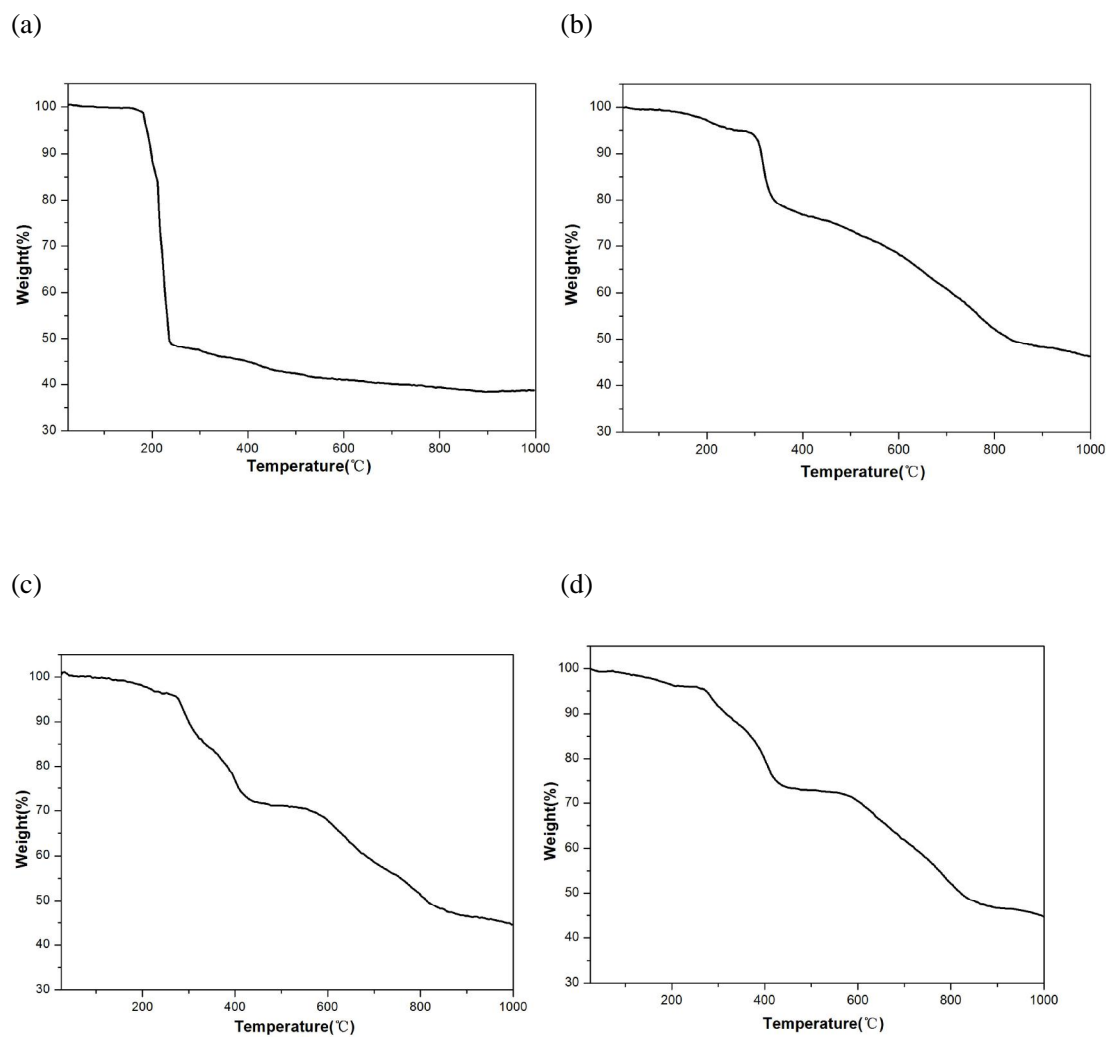
(c)



(d)

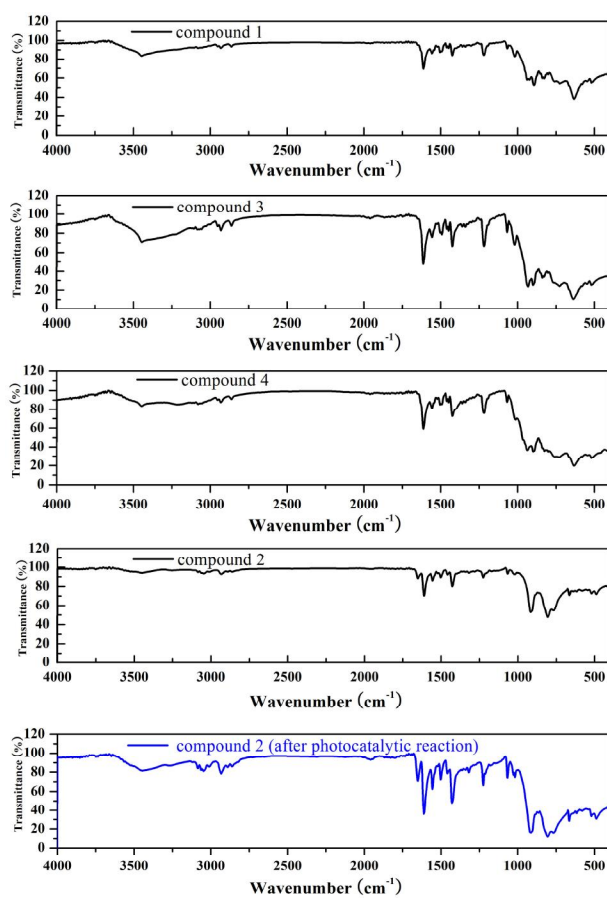


**Fig. S1** Experimental (red), simulated (black) and the experimental after photocatalytic reaction (blue) PXRD patterns for compound **1**(a); compound **2** (b); compound **3** (c); compound **4** (d).

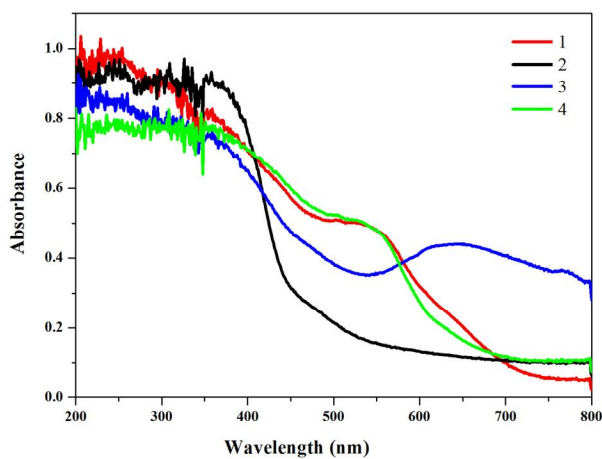


**Fig. S2** The TGA curves for compound **1**(a); compound **2** (b); compound **3** (c); compound **4** (d).

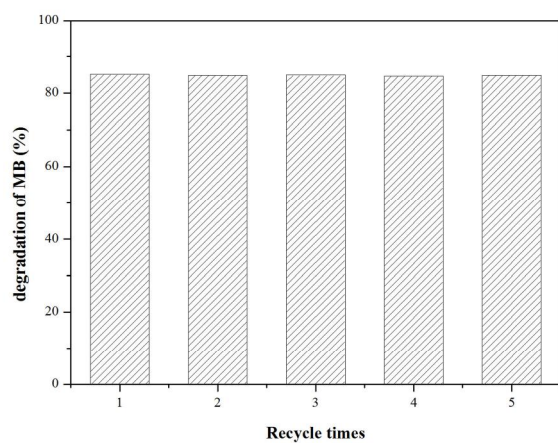




**Fig. S3** The IR spectra of compounds 1–4 (black ) and compound 2 after photocatalytic reaction (blue).



**Fig. S4** The UV spectra of compounds 1-4.



**Fig. S5** The recycle times on the MB degradation with compound **2** as catalyst.