Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Immobilization of enzyme on an organic-inorganic hybrid network consisting of Dawson-type polyoxotungstate and zinc(II)-biimidazole complex Moiety

Hao-Tian Zhu[a], Jing Du[a], Ying Lu[b], Fang Su[b], and Yangguang Li[*a]

Contents

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1. Crystal structure figures

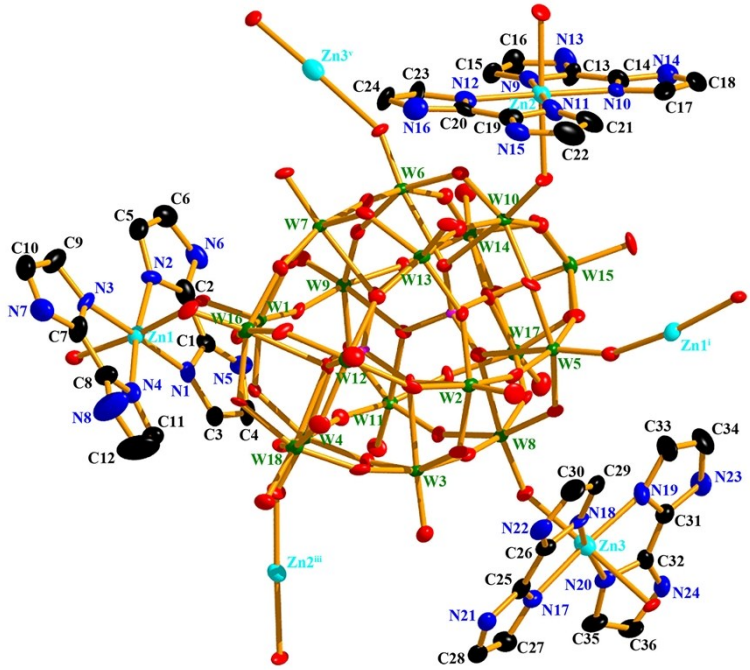

Fig. S1 ORTEP view of the asymmetric unit of compound **1** with atom labeling (30 % probability displacement ellipsoids; Hydrogen atoms and water molecules have been omitted for clarity)

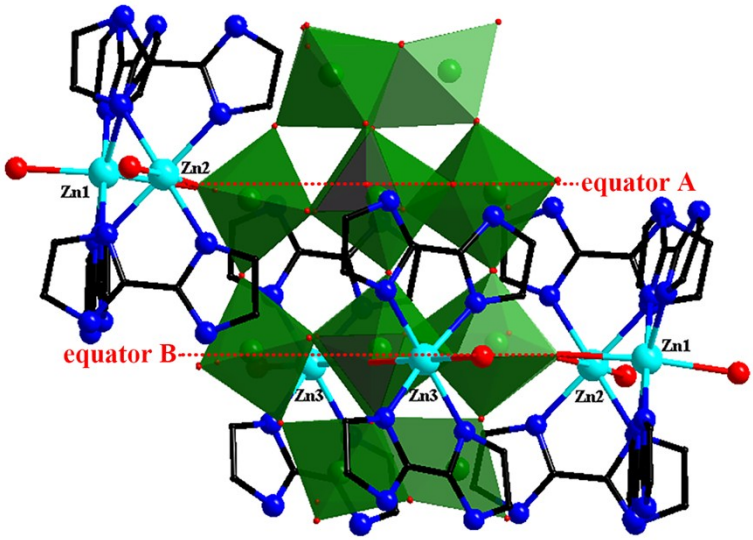

Fig. S2 Connection mode between Dawson-type POM and six Zn-H_2biim coordination units in compound **1**

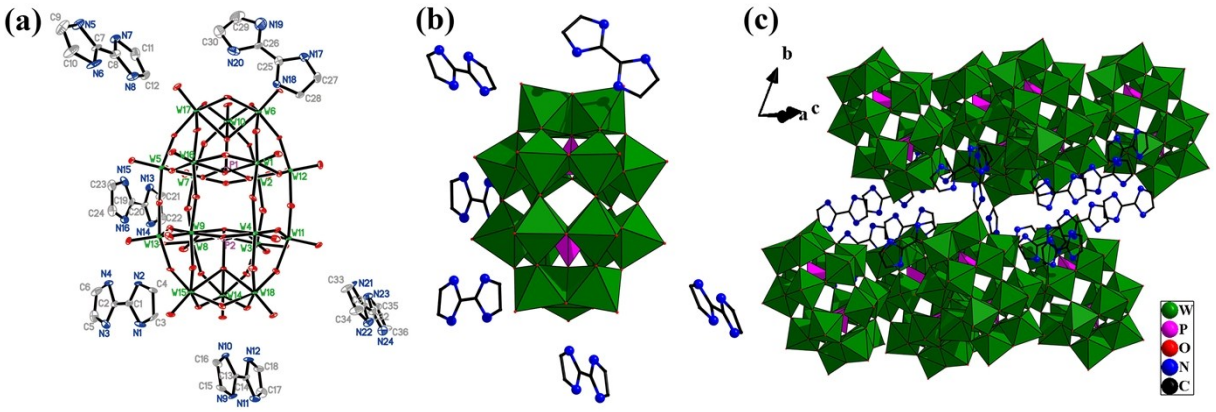

Fig. S3 Crystal structure of compound **2**. **(a)** ORTEP view of the asymmetric unit of compound **2** with atom labeling (30 % probability displacement ellipsoids); **(b)** Polyhedral and ball-and-stick representation of the basic building units in compound **2**; **(c)** The 3-D structure of compound **2** (free H_2O molecules, and hydrogen atoms are omitted for clarity)

2. Selected bond lengths and angles of compounds 1 and 2

Table S1 Selected bond lengths (Å) and angles (°) for compound **1**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1-O59	1.724(9)	W8-O26	1.912(11)	W16-O56	1.723(10)
W1-O29	1.882(10)	W8-O16	1.916(9)	W16-O60	1.890(11)
W1-O23	1.909(10)	W8-O53	2.370(9)	W16-O13	1.927(9)
W1-O2	1.921(9)	W9-O49	1.707(10)	W16-O10	1.927(9)
W1-O60	1.925(11)	W9-O23	1.889(10)	W16-O58	1.950(10)
W1-O8	2.346(9)	W9-O20	1.913(9)	W16-O36	2.392(9)
W2-O46	1.692(10)	W9-O9	1.914(10)	W17-O44	1.698(12)
W2-O43	1.892(9)	W9-O62	1.915(9)	W17-O21	1.908(8)
W2-O40	1.894(10)	W9-O11	2.383(9)	W17-O27	1.913(10)
W2-O32	1.915(9)	W10-O5	1.711(9)	W17-O1	1.913(10)
W2-O47	1.965(11)	W10-O24	1.878(10)	W17-O45	1.913(10)
W2-O12	2.396(9)	W10-O31	1.886(11)	W17-O28	2.398(10)
W3-O42	1.702(10)	W10-O4	1.899(9)	W18-O22	1.735(10)
W3-O26	1.891(11)	W10-O50	1.937(10)	W18-O54	1.891(10)
W3-O52	1.899(10)	W10-O55	2.356(9)	W18-O34	1.897(10)
W3-O43	1.908(10)	W11-O39	1.701(10)	W18-O19	1.917(10)
W3-O54	1.962(10)	W11-O7	1.896(10)	W18-O10	1.919(10)
W3-O12	2.387(9)	W11-O62	1.896(9)	W18-O36	2.367(9)
W4-O38	1.732(9)	W11-O6	1.920(9)	P1-O55	1.525(10)
W4-O52	1.881(9)	W11-O21	1.923(9)	P1-O11	1.528(9)
W4-O2	1.887(9)	W11-O11	2.365(9)	P1-O53	1.547(10)
W4-O7	1.901(10)	W12-O35	1.718(12)	P1-O28	1.592(10)
W4-O34	1.930(10)	W12-O58	1.896(9)	P2-O12	1.505(9)
W4-O8	2.366(9)	W12-O15	1.904(9)	P2-O51	1.519(10)
W5-O57	1.721(9)	W12-O19	1.922(10)	P2-O8	1.534(10)
W5-O47	1.834(10)	W12-O40	1.947(10)	P2-O36	1.580(10)
W5-O4	1.896(10)	W12-O36	2.398(10)	Zn1-O57#1	2.182(9)
W5-O16	1.896(9)	W13-O37	1.689(9)	Zn1-O59	2.314(9)
W5-O41	1.965(11)	W13-O32	1.866(9)	Zn1-N1	2.095(14)
W5-O53	2.336(9)	W13-O31	1.912(11)	Zn1-N2	2.125(13)
W6-O61	1.710(9)	W13-O15	1.917(9)	Zn1-N3	2.067(14)
W6-O9	1.878(9)	W13-O14	1.941(10)	Zn1-N4	2.159(15)
W6-O33	1.892(11)	W13-O51	2.402(9)	Zn2-O38#2	2.209(10)
W6-O24	1.920(10)	W14-O48	1.686(10)	Zn2-O5	2.323(9)
W6-O18	1.943(10)	W14-O18	1.885(10)	Zn2-N9	2.096(16)
W6-O55	2.408(9)	W14-O25	1.898(9)	Zn2-N10	2.116(13)
W7-O3	1.710(9)	W14-O20	1.950(9)	Zn2-N11	2.101(15)
W7-O33	1.904(10)	W14-O1	1.972(10)	Zn2-N12	2.125(13)

W7-O14	1.907(10)	W14-O28	2.375(9)	Zn3-O30	2.267(10)
W7-O13	1.913(9)	W15-O17	1.733(9)	Zn3-O61	2.566(10)
W7-O29	1.926(10)	W15-O41	1.873(10)	Zn3-N17	2.117(13)
W7-O51	2.351(9)	W15-O50	1.889(10)	Zn3-N18	2.025(14)
W8-O30	1.726(9)	W15-O45	1.936(11)	Zn3-N19	2.162(14)
W8-O6	1.878(9)	W15-O25	1.948(10)	Zn3-N20	2.073(13)
W8-O27	1.910(10)	W15-O28	2.368(8)		

Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
O59-W1-O29	104.5(4)	O27-W8-O26	162.9(4)	O56-W16-O60	102.0(5)
O59-W1-O23	98.7(4)	O6-W8-O16	156.9(4)	O56-W16-O13	101.9(4)
O29-W1-O2	156.7(4)	O49-W9-O23	98.8(4)	O13-W16-O10	156.3(4)
O23-W1-O60	164.6(4)	O23-W9-O20	163.3(4)	O60-W16-O58	156.6(4)
O46-W2-O43	101.0(5)	O49-W9-O9	102.9(4)	O44-W17-O21	103.7(5)
O46-W2-O40	99.5(5)	O9-W9-O62	157.5(4)	O21-W17-O27	85.1(4)
O43-W2-O32	156.3(4)	O5-W10-O24	99.5(4)	O27-W17-O1	156.4(4)
O40-W2-O47	161.5(4)	O5-W10-O31	98.4(5)	O44-W17-O28	170.7(4)
O42-W3-O26	98.4(5)	O24-W10-O4	156.8(4)	O22-W18-O54	103.1(4)
O42-W3-O52	103.1(5)	O31-W10-O50	164.5(4)	O22-W18-O34	103.9(5)
O52-W3-O43	156.5(4)	O39-W11-O7	100.3(4)	O34-W18-O19	156.8(4)
O26-W3-O54	165.5(4)	O39-W11-O62	99.2(4)	O54-W18-O10	158.7(4)
O38-W4-O52	103.6(4)	O62-W11-O6	157.4(4)	N3-Zn1-N1	177.0(5)
O38-W4-O2	100.0(4)	O7-W11-O21	163.1(4)	N3-Zn1-N2	103.3(5)
O38-W4-O7	99.6(5)	O35-W12-O58	99.8(5)	N3-Zn1-O57#1	89.9(4)
O7-W4-O34	164.9(4)	O58-W12-O15	90.5(4)	O57#1-Zn1-O59	171.1(3)
O57-W5-O47	98.3 (4)	O15-W12-O19	154.4(4)	N9-Zn2-N11	179.2(5)
O57-W5-O4	103.6(4)	O35-W12-O36	171.6(4)	N9-Zn2-N10	80.0(5)
O57-W5-O16	97.6(4)	O37-W13-O32	103.0(4)	N9-Zn2-O38#2	88.7(5)
O47-W5-O41	163.7(4)	O37-W13-O31	100.4(4)	O38#2-Zn2-O5	177.4(4)
O61-W6-O9	103.8(4)	O31-W13-O15	161.8(4)	N18-Zn3-N20	166.4(5)
O61-W6-O33	100.0(5)	O32-W13-O14	157.3(4)	N18-Zn3-N17	81.9(5)
O9-W6-O24	154.8(4)	O48-W14-O18	104.6(5)	N18-Zn3-O30	96.0(4)
O33-W6-O18	162.9(4)	O18-W14-O25	91.8(4)	O30-Zn3-O61	178.3(4)
O3-W7-O33	98.6(4)	O25-W14-O20	156.1(4)	O55-P1-O11	112.8(5)
O3-W7-O14	97.1(4)	O48-W14-O28	168.7(4)	O11-P1-O53	110.9(5)
O33-W7-O13	164.1(4)	O17-W15-O41	103.2(5)	O55-P1-O28	106.3(5)
O3-W7-O51	171.5(4)	O17-W15-O50	105.5(5)	O12-P2-O51	111.1(5)
O30-W8-O6	103.5(4)	O50-W15-O45	156.8(4)	O12-P2-O36	106.6(5)
O30-W8-O27	98.4(4)	O17-W15-O25	157.1(4)	O8-P2-O36	106.8(5)

Symmetry transformations used to generate equivalent atoms: #1 x-1, y-1, z; #2 x, y+1, z

Table S2 Hydrogen bonds for compound **1**

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N5-H5A…O3W	0.86	2.27	3.08(2)	155.3
N5-H5A…O44#4	0.86	2.44	2.940(19)	117.2
N6-H6A…O3W	0.86	2.16	2.97(2)	155.8
N7-H7A…O22#5	0.86	2.33	3.10(2)	149.3
N7-H7A…O4W#5	0.86	2.65	3.20(2)	123.3
N8-H8A…O22#5	0.86	2.25	2.06(2)	156.0
N8-H8A…O10#5	0.86	2.57	3.19(2)	129.2
N13-H13A…O1#6	0.86	2.00	2.790(19)	152.3
N13-H13A…O48#6	0.86	2.61	3.21(2)	128.1
N14-H14A…O1W	0.86	2.15	2.91(2)	147.5
N15-H15A…O5W	0.86	1.96	2.81(2)	168.5
N16-H16A…O56#7	0.86	2.16	2.909(19)	145.2
N21-H21A…O2W	0.86	2.10	2.95(2)	170.0
N22-H22A…O35#8	0.86	2.23	2.871(19)	131.2
N23-H23A…O17#9	0.86	2.33	3.088(19)	147.5
N23-H23A…O45#9	0.86	2.38	3.021(16)	131.4
N24-H24A…O17#9	0.86	1.96	2.791(16)	161.0

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

Table S3 Selected bond lengths (Å) and angles (°) for compound **2**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1-O43	1.715(11)	W7-O62	1.887(11)	W14-O25	1.692(12)
W1-O51	1.911(12)	W7-O28	1.936(12)	W14-O54	1.880(11)
W1-O6	1.921(12)	W7-O44	2.351(11)	W14-O26	1.912(10)
W1-O58	1.925(11)	W8-O29	1.692(12)	W14-O59	1.918(10)
W1-O22	1.932(12)	W8-O42	1.901(11)	W14-O23	1.936(12)
W1-O4	2.375(11)	W8-O11	1.907(12)	W14-O10	2.390(11)
W2-O7	1.708(12)	W8-O3	1.911(12)	W15-O34	1.714(12)
W2-O41	1.873(13)	W8-O54	1.938(11)	W15-O50	1.865(11)
W2-O19	1.906(11)	W8-O8	2.358(11)	W15-O24	1.895(12)
W2-O62	1.908(11)	W9-O27	1.693(11)	W15-O26	1.909(10)
W2-O2	1.940(11)	W9-O21	1.880(12)	W15-O49	1.937(12)
W2-O48	2.352(11)	W9-O20	1.911(11)	W15-O10	2.399(10)
W3-O38	1.710(12)	W9-O24	1.921(12)	W16-O39	1.721(11)
W3-O59	1.887(11)	W9-O60	1.924(11)	W16-O36	1.862(11)
W3-O42	1.902(12)	W9-O61	2.376(10)	W16-O20	1.876(11)
W3-O31	1.908(11)	W10-O45	1.709(11)	W16-O51	1.922(11)
W3-O41	1.926(12)	W10-O28	1.883(11)	W16-O30	1.954(11)

W3-O53	2.377(10)	W10-O2	1.887(10)	W16-O4	2.356(11)
W4-O17	1.709(12)	W10-O16	1.935(11)	W17-O57	1.708(13)
W4-O6	1.874(12)	W10-O37	1.940(10)	W17-O30	1.897(12)
W4-O60	1.898(11)	W10-O9	2.337(11)	W17-O16	1.904(11)
W4-O52	1.916(12)	W11-O13	1.704(12)	W17-O14	1.914(11)
W4-O33	1.928(12)	W11-O18	1.863(12)	W17-O32	1.934(11)
W4-O61	2.353(10)	W11-O52	1.880(12)	W17-O9	2.390(11)
W5-O35	1.697(12)	W11-O47	1.938(11)	W18-O55	1.682(11)
W5-O14	1.901(11)	W11-O31	1.946(11)	W18-O47	1.869(11)
W5-O5	1.918(12)	W11-O53	2.377(10)	W18-O33	1.887(12)
W5-O46	1.919(11)	W12-O56	1.702(11)	W18-O23	1.938(12)
W5-O36	1.926(11)	W12-O58	1.878(11)	W18-O49	1.970(11)
W5-O44	2.376(10)	W12-O1	1.900(11)	W18-O10	2.376(11)
W6-O12	1.705(11)	W12-O18	1.923(12)	P1-O4	1.525(11)
W6-O32	1.894(12)	W12-O19	1.925(11)	P1-O48	1.526(12)
W6-O22	1.894(12)	W12-O48	2.381(11)	P1-O44	1.547(10)
W6-O37	1.906(10)	W13-O15	1.710(11)	P1-O9	1.594(12)
W6-O1	1.919(10)	W13-O5	1.884(12)	P2-O53	1.512(11)
W6-O9	2.390(10)	W13-O21	1.896(11)	P2-O8	1.531(11)
W7-O40	1.707(11)	W13-O11	1.911(12)	P2-O61	1.539(11)
W7-O3	1.881(12)	W13-O50	1.969(11)	P2-O10	1.564(11)
W7-O46	1.887(12)	W13-O8	2.377(10)		

Bond	Angle(°)	Bond	Angle(°)	Bond	Angle(°)
O43-W1-O51	100.2(5)	O40-W7-O44	174.4(5)	O54-W14-O59	84.9(5)
O43-W1-O6	98.1(5)	O46-W7-O44	73.6(4)	O54-W14-O23	155.9(5)
O51-W1-O58	157.2(4)	O42-W8-O11	157.2(5)	O59-W14-O23	87.6(5)
O6-W1-O22	163.8(5)	O42-W8-O54	86.0(5)	O25-W14-O10	171.5(5)
O7-W2-O41	100.8(6)	O3-W8-O54	164.9(5)	O50-W15-O24	86.5(5)
O7-W2-O19	99.3(6)	O11-W8-O8	73.5(4)	O24-W15-O26	157.3(5)
O19-W2-O62	157.7(5)	O21-W9-O24	85.5(5)	O26-W15-O49	86.3(5)
O41-W2-O2	176.0(5)	O20-W9-O24	162.5(5)	O34-W15-O10	168.0(5)
O38-W3-O59	97.4(5)	O21-W9-O60	156.9(5)	O20-W16-O30	163.9(5)
O38-W3-O42	102.2(5)	O24-W9-O61	81.5(4)	O39-W16-O4	171.7(5)
O42-W3-O31	157.4(5)	O28-W10-O37	158.2(5)	O20-W16-O4	83.7(4)
O59-W3-O41	163.6(5)	O45-W10-O9	170.6(5)	O51-W16-O4	72.9(4)
O17-W4-O6	99.1(6)	O28-W10-O9	85.1(4)	O30-W17-O16	155.5(5)
O17-W4-O60	99.8(6)	O16-W10-O9	72.9(4)	O16-W17-O32	87.3(5)
O60-W4-O52	157.5(5)	O18-W11-O47	164.1(5)	O57-W17-O9	170.8(5)
O6-W4-O33	163.7(5)	O47-W11-O31	87.5(5)	O14-W17-O9	84.1(4)
O14-W5-O5	162.8(5)	O13-W11-O53	172.1(5)	O47-W18-O49	157.1(5)
O14-W5-O36	85.8(5)	O52-W11-O53	84.3(4)	O33-W18-O49	88.8(5)

O5-W5-O36	87.5(5)	O58-W12-O18	87.1(5)	O55-W18-O10	168.0(5)
O35-W5-O44	173.5(5)	O1-W12-O18	163.8(50	O23-W18-O10	73.3(4)
O32-W6-O22	88.2(5)	O56-W12-O48	173.8(5)	O4-P1-O48	112.0(6)
O32-W6-O1	156.9(4)	O19-W12-O48	72.7(4)	O48-P1-O44	112.2(6)
O12-W6-O9	171.9(5)	O5-W13-O50	162.3(4)	O4-P1-O9	106.7(6)
O37-W6-O9	72.5(4)	O21-W13-O50	83.2(5)	O53-P2-O8	112.3(6)
O3-W7-O62	88.9(5)	O15-W13-O8	173.4(5)	O53-P2-O61	111.5(6)
O3-W7-O28	164.1(5)	O11-W13-O8	72.9(4)	O8-P2-O10	106.1(6)

Table S4 Hydrogen bonds for compound **2**

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N1-H1A…O45#1	0.86	1.99	2.82(2)	161.7
N2-H2A…O39#2	0.86	2.17	2.918(19)	145.9
N2-H2A…O27	0.86	2.39	2.903(19)	118.7
N3-H3B…O8W	0.86	2.45	3.14(3)	137.9
N4-H4B…O39#2	0.86	2.24	2.94(2)	138.2
N4-H4B…O15	0.86	2.48	3.00()2	119.8
N6-H6B…O1W#2	0.86	2.10	2.92(2)	158.0
N6-H6B…O29#2	0.86	2.56	3.06(2)	117.9
N8-H8A…O1W#2	0.86	2.02	2.84(2)	160.9
N9-H9B…O3W	0.86	1.94	2.79(2)	172.8
N10-H10B…O49	0.86	1.88	2.732(19)	168.8
N11-H11B…O3W	0.86	2.24	3.06(3)	159.6
N12-H12B…O23	0.86	2.02	2.82(2)	154.3
N13-H13A…O5W	0.86	2.20	3.00(3)	154.0
N13-H13A…O55#3	0.86	2.38	2.90(2)	119.0
N14-H14A…O1W	0.86	1.86	2.71(2)	168.7
N15-H15B…O5W	0.86	1.85	2.70(3)	168.4
N16-H16B…O1W	0.86	2.21	3.01(3)	154.9
N16-H16B…O56#4	0.86	2.56	3.06(3)	118.4
N17-H17B…O7W	0.86	2.16	2.94(3)	150.1
N18-H18B…O2W	0.86	1.94	2.777(19)	164.0
N19-H19A…O7W	0.86	2.11	2.87(3)	147.8
N19-H19A…O7W#5	0.86	2.55	3.04(3)	116.9
N20-H20A…O2W	0.86	2.05	2.87(3)	159.2
N21-H21B…O4W	0.86	2.22	3.01(3)	151.1
N21-H22B…O13	0.86	2.32	2.84(2)	119.5
N23-H23B…O4W	0.86	1.91	2.75(3)	166.1

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

3. Physical characterizations

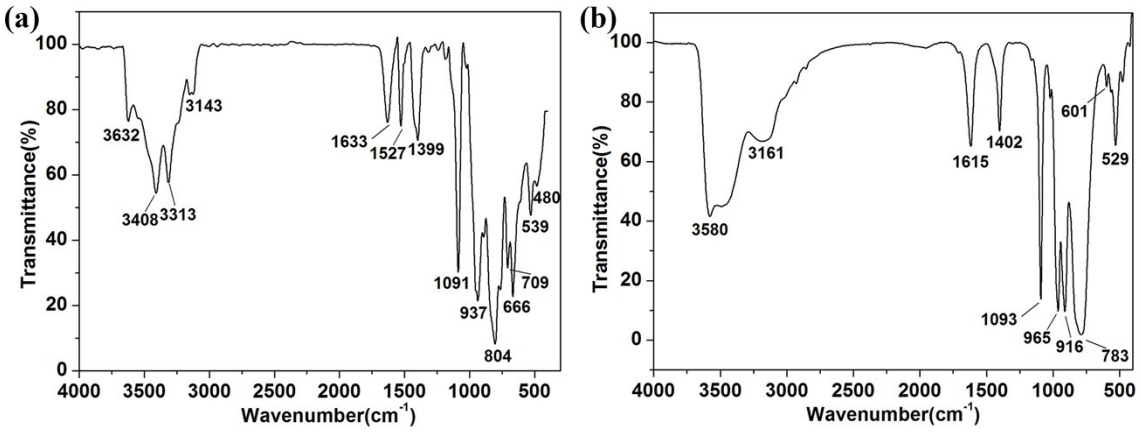

Fig. S4 IR spectra of **(a)** compound **1** and **(b) K-{P_2W_{18}}**

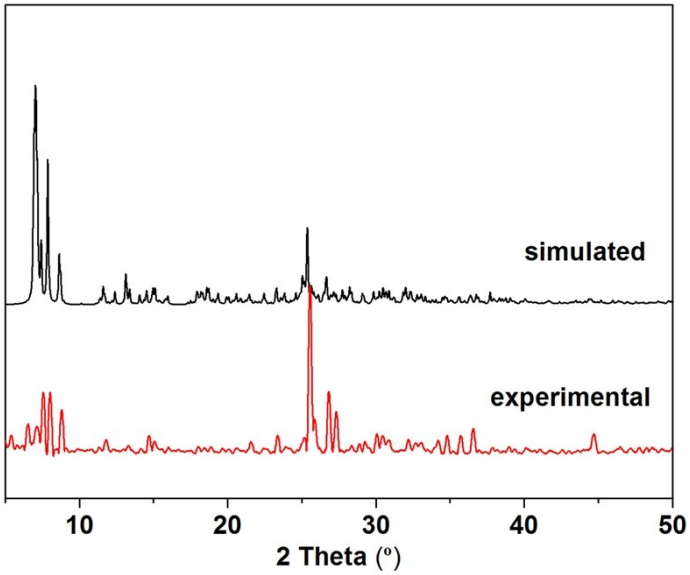

Fig. S5 The simulated and experimental XRD patterns of compound **1**

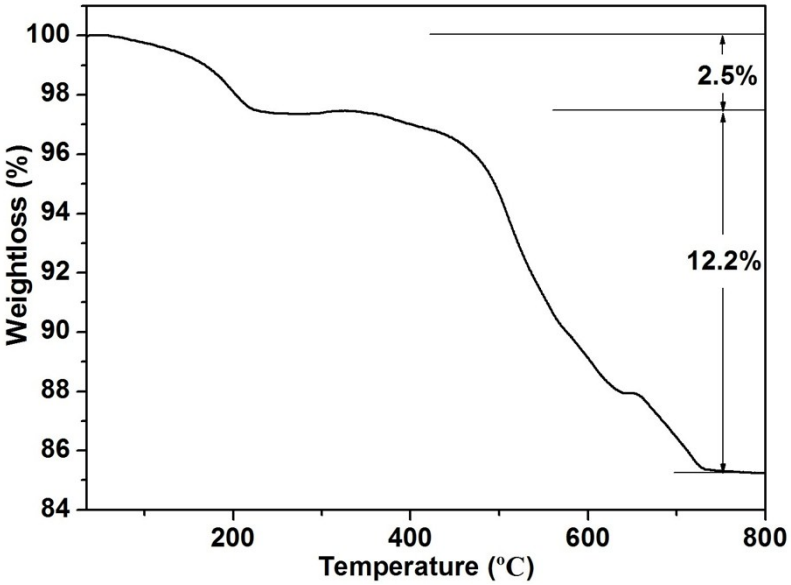

Fig. S6 TG curve of compound **1**

4. Enzyme immobilization

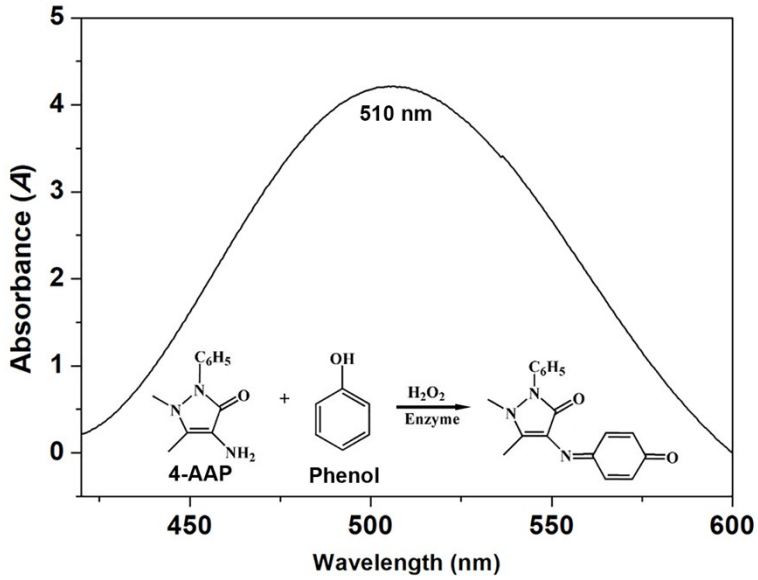

Fig. S7 The UV-vis absorption spectrum of co-oxidation reaction solution of 4-AAP and phenol catalyzed by enzyme

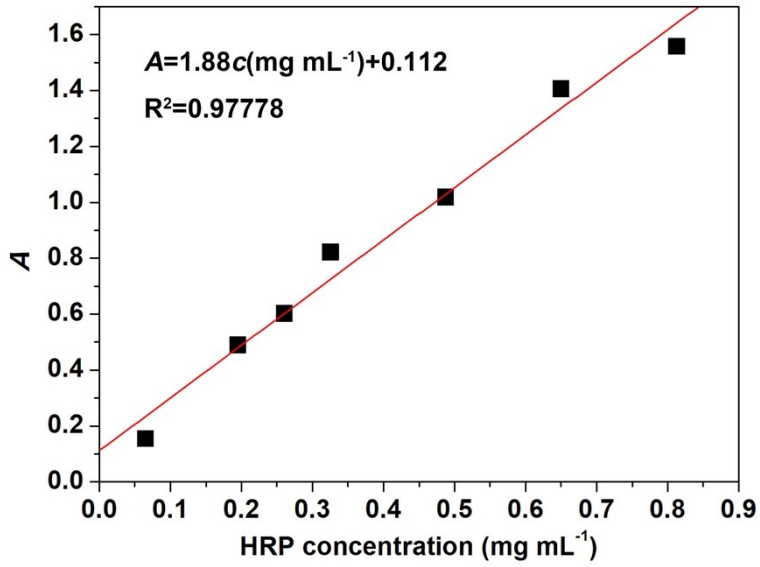

Fig. S8 The standard curve of HRP

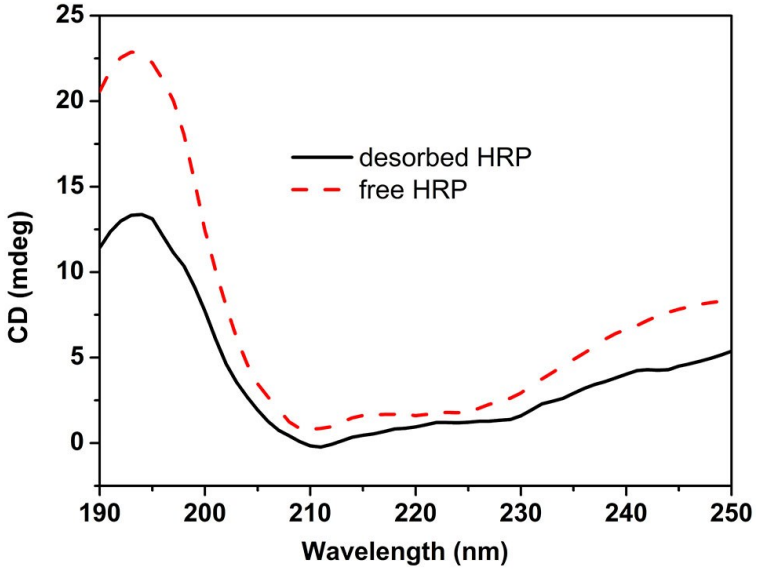

Fig. S9 CD spectra of free HRP and desorbed HRP from HRP/**1**

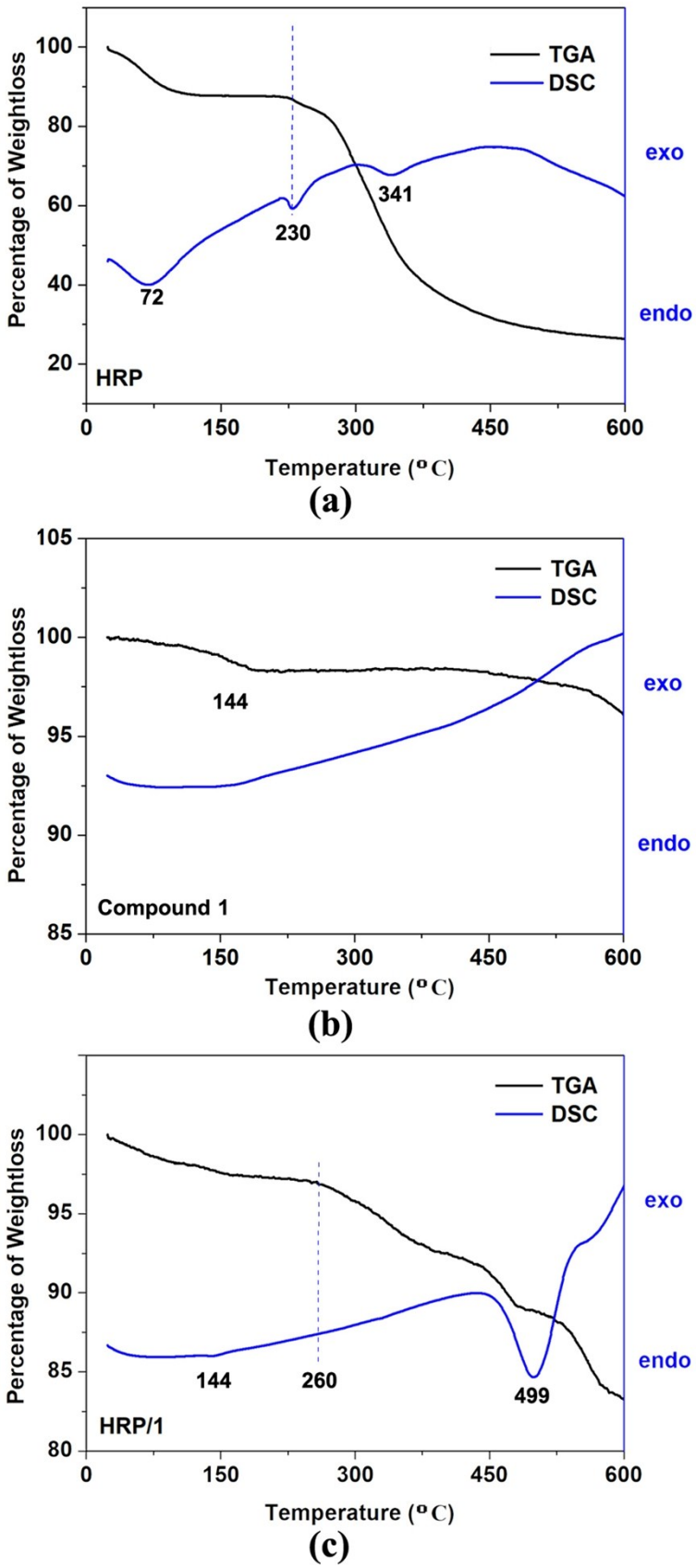

Fig. S10 The TGA and DSC curves of (a) HRP; (b) compound **1**; (c) HRP/**1** in nitrogen atmosphere.

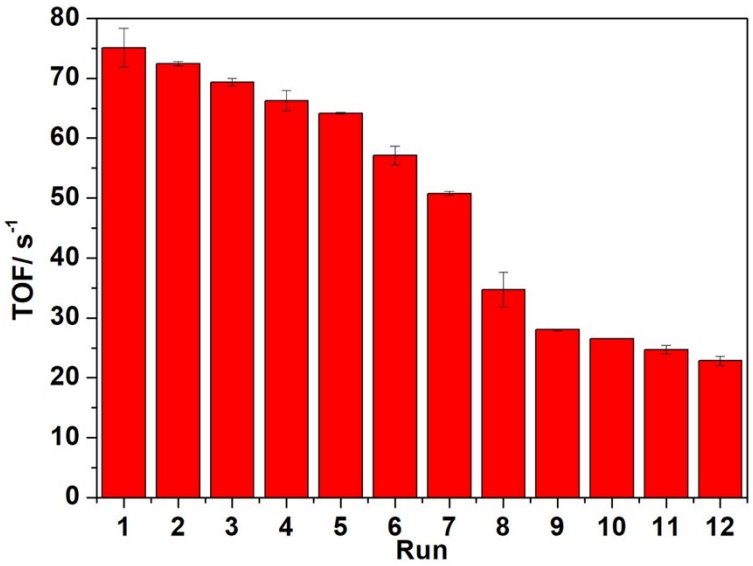

Fig. S11 The reusability of immobilized enzyme HRP/**1** (HRP loading of 90.1 mg g^{-1}) as a catalyst for co-oxidation of phenol and 4-AAP at pH 6

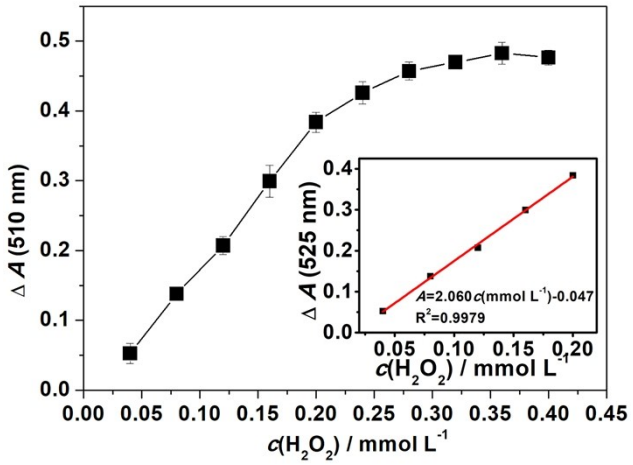

Fig. S12 The linear calibration plot for H_2O_2 detection by the reuse of HRP/**1** after six recycles as catalyst. Δ*A* = *A* (the immobilized HRP, 510 nm) − *A* (blank, 510 nm). Reaction time is 5 min (Inset: Kinetics curve)