

Supporting Information

Inhibitory Effects of Substituted Different Transition Metal-Based Krebs-type Sandwich Structure on Human Hepatocellular Carcinoma cells

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Table S1 Crystal data and refinement parameters for Compounds **3** and **4**.

Compound	3	4
Empirical formula	C ₆ H ₈₂ Bi ₂ N ₄ Na ₄ Ni ₃ O _{105.5} W ₁₉	C ₆ H ₇₄ Bi ₂ N ₄ Na ₄ O ₁₀₁ W ₂₀ Zn ₂
Formula weight	6077.96	6136.20
Temperature, K	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	P -1	P -1
a, Å	12.4706(5)	12.549(5)
b, Å	13.6489(5)	13.769(5)
c, Å	16.9382(6)	17.098(6)
α, deg	69.435(3)	68.787(5)
β, deg	82.923(3)	83.447(5)
γ, deg	64.629(4)	65.422(4)
Volume, Å ³	2437.71(18)	2502.3(16)
Z	1	1
D _{calcd} (g cm ⁻³)	4.141	4.072
μ(Mo Kα), mm ⁻¹	26.617	26.986
F(000)	2690	2696
Reflections collected/unique (R _{int})	30014 / 9943	15227 / 11678
GOF on F ²	1.060	1.095
Final R indices [I > 2σ(I)]	R1 = 0.0389, wR2 = 0.0927	R1 = 0.0783, wR2 = 0.1898
R (all data)	R1 = 0.0497, wR2 = 0.1095	R1 = 0.1491, wR2 = 0.2304

(* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (wF_o^2)^2]^{1/2}$).

Table S2: Selected bond lengths (Å) and angles (deg) for Compound **3**.

W(1)-O(26)	1.752(10)	W(1)-O(32)	1.807(10)	W(1)-O(17)	2.072(9)
W(1)-O(9)	1.797(10)	W(1)-O(31)	2.070(9)	W(1)-O(13)	2.229(9)
W(2)-O(4)	1.723(10)	W(2)-O(33)	1.884(11)	W(2)-O(34)	1.937(10)
W(2)-O(16)	1.884(10)	W(2)-O(15)	1.902(10)	W(2)-O(10)	2.288(9)
W(3)-O(19)	1.720(9)	W(3)-O(31)	1.880(9)	W(3)-O(7)	1.984(10)
W(3)-O(20)	1.887(10)	W(3)-O(16)	1.980(10)	W(3)-O(13)	2.304(9)
W(4)-O(3)	1.728(10)	W(4)-O(34)	1.946(10)	W(4)-O(20)	1.948(10)
W(4)-O(11)	1.843(9)	W(4)-O(2)	1.898(10)	W(4)-O(10)	2.239(9)
W(5)-O(24)	1.743(11)	W(5)-O(27)	1.931(9)	W(5)-O(25)	2.033(10)
W(5)-O(5)	1.775(10)	W(5)-O(21)	1.964(10)	W(5)-O(12)	2.199(10)
W(6)-O(23)	1.735(11)	W(6)-O(27)	1.917(10)	W(6)-O(33)	2.055(10)
W(6)-O(22)	1.776(10)	W(6)-O(2)	1.960(10)	W(6)-O(10)	2.206(10)
W(7)-O(6)	1.704(10)	W(7)-O(29)	1.900(10)	W(7)-O(30)	1.953(9)
W(7)-O(25)	1.890(11)	W(7)-O(15)	1.926(10)	W(7)-O(12)	2.277(9)
W(8)-O(18)	1.718(10)	W(8)-O(7)	1.904(9)	W(8)-O(29)	1.946(10)
W(8)-O(17)	1.877(9)	W(8)-O(14)	1.916(10)	W(8)-O(13)	2.297(9)
W(9)-O(8)	1.726(10)	W(9)-O(14)	1.932(10)	W(9)-O(30)	1.942(9)
W(9)-O(28)	1.857(10)	W(9)-O(21)	1.936(11)	W(9)-O(12)	2.246(9)
W(10)-O(1)	1.869(12)	W(10)-O(28)	1.979(10)	W(10)-O(9)	2.075(10)
W(10)-O(35)	1.899(14)	W(10)-O(11)#1	2.014(10)	W(10)-O(32)#1	2.089(10)
Ni(1)-O(1W)	1.860(11)	Ni(1)-O(35)	1.895(12)	Ni(1)-O(28)	1.979(9)
Ni(1)-O(11) #1	2.017(9)	Ni(1)-O(9)	2.070(10)	Ni(1)-O(32) #1	2.083(10)
Ni(2)-O(26)	2.032(10)	Ni(2)-O(8W)	1.943(13)	Ni(2)-O(5)#1	2.033(10)
Ni(2)-O(22)#1	2.071(10)	Ni(2)-O(7W)	2.077(12)	Ni(2)-O(10W)	2.113(12)
Bi(1)-O(13)	2.107(9)	Bi(1)-O(10)	2.136(8)	Bi(1)-O(12)	2.140(9)
Na(1)-O(4)	2.282(12)	Na(1)-O(11W)	2.346(17)	Na(1)-O(3W)	2.469(13)
Na(1)-O(19) #1	2.353(12)	Na(1)-O(4W)	2.434(14)	Na(1)-O(5W)	2.476(14)
Na(2)-O(3w)	2.327(14)	Na(2)-O(6W)	2.361(15)	Na(2)-O(2w)	2.427(13)
Na(2)-O(9W)	2.390(15)	Na(2)-O(4W)	2.418(14)	Na(2)-O(5W)	2.408(13)
O(26)-W(1)-O(9)	102.6(5)	O(26)-W(1)-O(32)	103.0(5)	O(26)-W(1)-O(31)	94.5(4)
O(26)-W(1)-O(17)	96.4(4)	O(26)-W(1)-O(13)	163.8(4)	O(4)-W(2)-O(16)	102.4(5)
O(4)-W(2)-O(33)	100.2(5)	O(4)-W(2)-O(15)	99.6(5)	O(4)-W(2)-O(34)	97.9(5)
O(4)-W(2)-O(10)	170.6(4)	O(19)-W(3)-O(20)	101.6(4)	O(19)-W(3)-O(31)	99.3(4)
O(19)-W(3)-O(16)	100.9(4)	O(19)-W(3)-O(7)	96.4(4)	O(19)-W(3)-O(13)	168.7(4)
O(3)-W(4)-O(11)	103.1(5)	O(3)-W(4)-O(2)	101.1(5)	O(3)-W(4)-O(34)	100.2(4)
O(3)-W(4)-O(20)	100.0(5)	O(3)-W(4)-O(10)	173.7(4)	O(24)-W(5)-O(25)	96.9(5)
O(24)-W(5)-O(5)	104.0(5)	O(24)-W(5)-O(27)	100.2(5)	O(24)-W(5)-O(21)	96.5(5)
O(24)-W(5)-O(12)	167.0(4)	O(23)-W(6)-O(22)	105.0(5)	O(23)-W(6)-O(27)	103.2(5)
O(23)-W(6)-O(2)	95.2(5)	O(23)-W(6)-O(33)	94.1(5)	O(23)-W(6)-O(10)	162.5(4)
O(6)-W(7)-O(25)	101.1(5)	O(6)-W(7)-O(29)	101.6(5)	O(6)-W(7)-O(15)	100.2(5)
O(6)-W(7)-O(30)	97.9(5)	O(6)-W(7)-O(12)	171.5(4)	O(18)-W(8)-O(17)	98.7(5)
O(18)-W(8)-O(7)	97.0(5)	O(18)-W(8)-O(14)	101.5(4)	O(18)-W(8)-O(29)	100.5(5)

O(18)-W(8)-O(13)	170.4(4)	O(8)-W(9)-O(28)	105.4(5)	O(8)-W(9)-O(14)	100.1(5)
O(8)-W(9)-O(21)	98.4(5)	O(8)-W(9)-O(30)	97.7(5)	O(8)-W(9)-O(12)	170.7(4)
O(1)-W(10)-O(35)	98.8(6)	O(1)-W(10)-O(28)	95.7(5)	O(1)-W(10)-O(11)	90.1(5)
O(1)-W(10)-O(9)	91.8(5)	O(1)-W(10)-O(32)	171.7(5)	O(8W)-Ni(2)-O(26)	88.6(5)
O(8W)-Ni(2)-O(5)#1	177.4(5)	O(8W)-Ni(2)-O(22)#1	100.1(5)	O(8W)-Ni(2)-O(7W)	83.3(6)
O(8W)-Ni(2)-O(10W)	87.2(6)	O(4)-Na(1)-O(19)	95.3(4)	O(4)-Na(1)-O(11W)	92.2(5)
O(4)-Na(1)-O(4W)	103.2(5)	O(4)-Na(1)-O(3W)	177.2(5)	O(4)-Na(1)-O(5W)	104.4(4)
O(3W)-Na(2)-O(9W)	85.3(5)	O(3W)-Na(2)-O(6W)	169.3(5)	O(3W)-Na(2)-O(4W)	80.5(5)
O(3W)-Na(2)-O(2W)	88.4(5)	O(3W)-Na(2)-O(5W)	82.6(5)		

Table S3: Selected bond lengths (Å) and angles (deg) for Compound **4**.

W(1)-O(3)	1.72(3)	W(1)-O(32)	1.76(3)	W(1)-O(6)	1.95(3)
W(1)-O(29)#1	2.01(2)	W(1)-O(19)	2.12(2)	W(1)-O(8)#1	2.14(3)
W(2)-O(23)	1.76(3)	W(2)-O(8)	1.80(3)	W(2)-O(19)	1.83(2)
W(2)-O(2)	2.02(3)	W(2)-O(21)	2.09(3)	W(2)-O(33)	2.22(3)
W(3)-O(28)	1.70(3)	W(3)-O(31)	1.90(2)	W(3)-O(18)	1.93(2)
W(3)-O(20)	1.92(2)	W(3)-O(10)	2.00(2)	W(3)-O(30)	2.34(3)
W(4)-O(11)	1.75(3)	W(4)-O(18)	1.91(2)	W(4)-O(4)	1.93(2)
W(4)-O(27)	1.93(2)	W(4)-O(1)	2.00(2)	W(4)-O(17)	2.00(2)
W(5)-O(34)	1.71(3)	W(5)-O(21)	1.87(3)	W(5)-O(9)	1.94(2)
W(5)-O(22)	1.94(2)	W(5)-O(4)	1.96(2)	W(5)-O(33)	2.35(3)
W(6)-O(35)	1.74(3)	W(6)-O(7)	1.78(3)	W(6)-O(15)	1.93(2)
W(6)-O(14)	1.99(2)	W(6)-O(31)	2.04(3)	W(6)-O(30)	2.24(2)
W(7)-O(26)	1.74(3)	W(7)-O(1)	1.88(3)	W(7)-O(6)	1.89(3)
W(7)-O(22)	1.92(2)	W(7)-O(16)	1.95(2)	W(7)-O(17)	2.25(2)
W(8)-O(24)	1.76(2)	W(8)-O(12)	1.82(3)	W(8)-O(15)	1.94(2)
W(8)-O(16)	2.00(2)	W(8)-O(27)	2.05(3)	W(8)-O(17)	2.17(2)
W(9)-O(25)	1.75(2)	W(9)-O(10)	1.90(3)	W(9)-O(29)	1.91(3)
W(9)-O(14)	1.90(2)	W(9)-O(13)	1.97(2)	W(9)-O(30)	2.28(2)
W(10)-O(5)	1.71(2)	W(10)-O(2)	1.84(3)	W(10)-O(13)	1.88(3)
W(10)-O(9)	1.95(3)	W(10)-O(20)	1.98(2)	W(10)-O(33)	2.29(2)
Zn(1)-O(2W)	1.97(3)	Zn(1)-O(12)	2.05(3)	Zn(1)-O(23)#1	2.12(3)
Zn(1)-O(3W)	2.145(18)	Zn(1)-O(1W)	2.10(3)	Zn(1)-O(7)	2.16(3)
Bi(1)-O(30)	2.09(3)	Bi(1)-O(33)	2.13(2)	Bi(1)-O(17)	2.18(2)
Na(1)-O(28)#2	2.35(3)	Na(1)-O(5)	2.38(3)	Na(1)-O(8W)	2.42(3)
Na(1)-O(4W)	2.31(3)	Na(1)-O(10W)	2.43(3)	Na(1)-O(9W)	2.69(3)
Na(2)-O(8W)	2.28(3)	Na(2)-O(5W)	2.33(5)	Na(2)-O(6W)	2.72(4)
Na(2)-O(10W)	2.40(3)	Na(2)-O(7W)	2.47(3)	Na(2)-O(9W)	2.74(3)
O(3)-W(1)-O(32)	102.9(12)	O(23)-W(2)-O(8)	100.0(12)	O(28)-W(3)-O(31)	101.2(12)
O(3)-W(1)-O(19)	91.1(11)	O(23)-W(2)-O(19)	103.2(11)	O(28)-W(3)-O(18)	102.3(11)
O(3)-W(1)-O(6)	95.8(12)	O(23)-W(2)-O(2)	96.1(11)	O(28)-W(3)-O(20)	101.1(11)
O(3)-W(1)-O(29)#1	93.1(11)	O(23)-W(2)-O(21)	96.9(11)	O(28)-W(3)-O(10)	95.8(11)
O(3)-W(1)-O(8)#1	168.1(11)	O(23)-W(2)-O(33)	164.7(11)	O(28)-W(3)-O(30)	170.0(11)
O(11)-W(4)-O(18)	100.5(11)	O(34)-W(5)-O(21)	98.6(12)	O(35)-W(6)-O(7)	104.3(12)
O(11)-W(4)-O(4)	100.3(11)	O(34)-W(5)-O(9)	97.1(12)	O(35)-W(6)-O(15)	101.6(11)
O(11)-W(4)-O(27)	99.2(11)	O(34)-W(5)-O(22)	102.0(11)	O(35)-W(6)-O(14)	95.4(11)
O(11)-W(4)-O(1)	98.2(11)	O(34)-W(5)-O(4)	98.1(12)	O(35)-W(6)-O(31)	93.5(11)
O(11)-W(4)-O(17)	169.8(10)	O(34)-W(5)-O(33)	169.8(10)	O(35)-W(6)-O(30)	163.8(11)
O(26)-W(7)-O(1)	99.3(12)	O(24)-W(8)-O(12)	104.2(12)	O(25)-W(9)-O(10)	100.9(11)
O(26)-W(7)-O(6)	102.8(12)	O(24)-W(8)-O(15)	101.0(11)	O(25)-W(9)-O(29)	102.8(11)
O(26)-W(7)-O(22)	99.6(11)	O(24)-W(8)-O(16)	94.3(11)	O(25)-W(9)-O(14)	100.4(10)
O(26)-W(7)-O(16)	98.7(11)	O(24)-W(8)-O(27)	95.8(11)	O(25)-W(9)-O(13)	100.0(10)
O(26)-W(7)-O(17)	171.8(10)	O(24)-W(8)-O(17)	164.9(11)	O(25)-W(9)-O(30)	175.5(10)

O(5)-W(10)-O(2)	101.0(11)	O(5)-W(10)-O(20)	100.7(11)	O(5)-W(10)-O(33)	169.7(10)
O(5)-W(10)-O(13)	101.6(11)	O(5)-W(10)-O(9)	96.6(12)	O(2W)-Zn(1)-O(12)	175.1(10)
O(2W)-Zn(1)-O(23)#1	87.5(11)	O(2W)-Zn(1)-O(3W)	93.0(10)	O(2W)-Zn(1)-O(1W)	87.0(11)
O(2W)-Zn(1)-O(7)	98.7(10)	O(28)#2-Na(1)-O(5)	96.1(10)	O(28)#2-Na(1)-O(8W)	177.6(12)
O(28)#2-Na(1)-O(4W)	95.6(14)	O(28)#2-Na(1)-O(10W)	102.3(11)	O(28)#2-Na(1)-O(9W)	92.8(10)
O(8W)-Na(2)-O(5W)	96.4(16)	O(8W)-Na(2)-O(6W)	159.9(11)	O(8W)-Na(2)-O(10W)	80.7(11)
O(8W)-Na(2)-O(7W)	88.0(11)	O(8W)-Na(2)-O(9W)	86.4(10)		

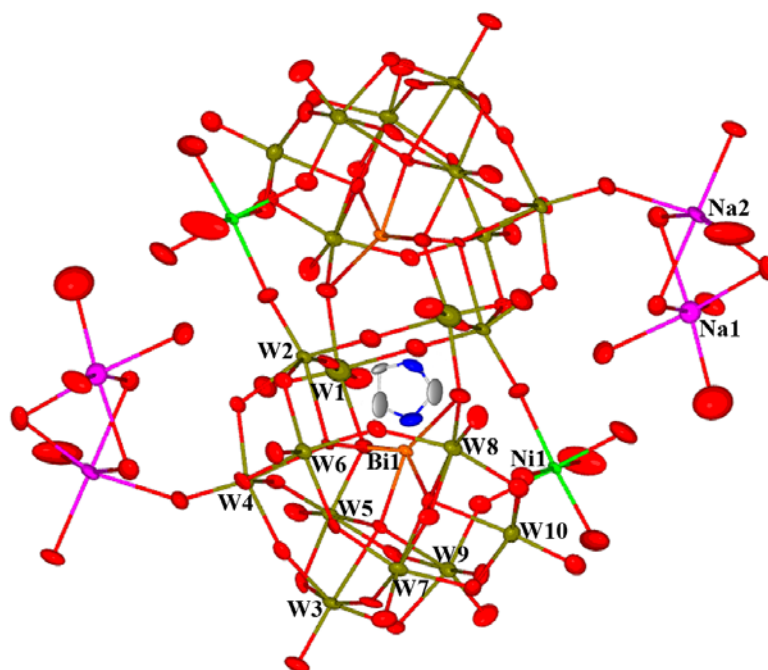


Figure S1. View of the molecule structure unit of compound **3**.

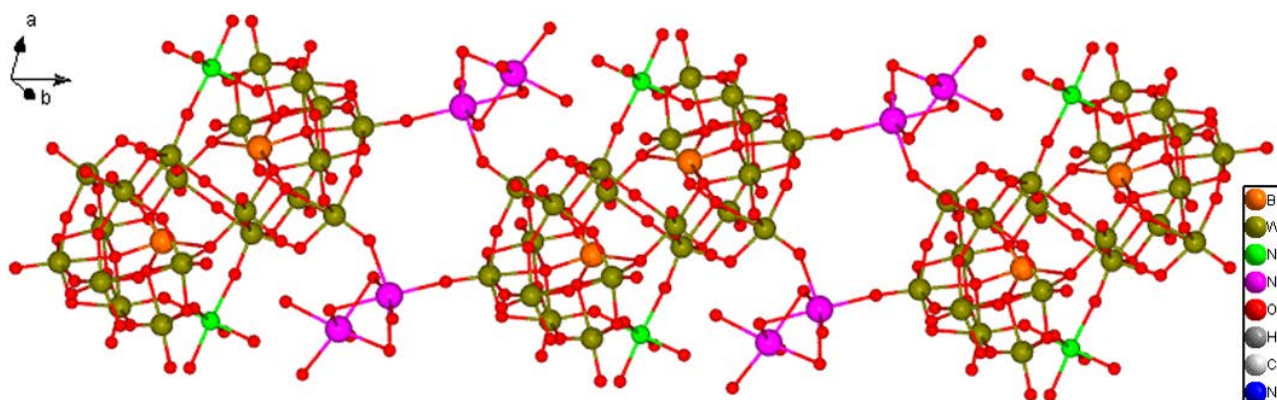


Figure S2. 1-D chain of compound **3** was made by sandwiched POM units and binuclear linkers $[\text{Na}_2(\text{H}_2\text{O})_7]$.

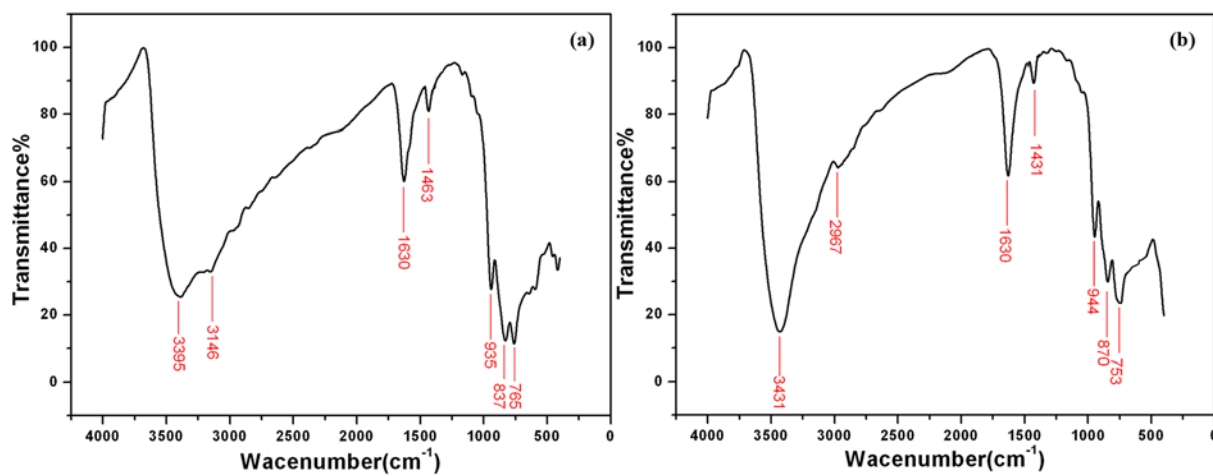


Figure S3. IR spectra of compounds **3** (a) and **4** (b).

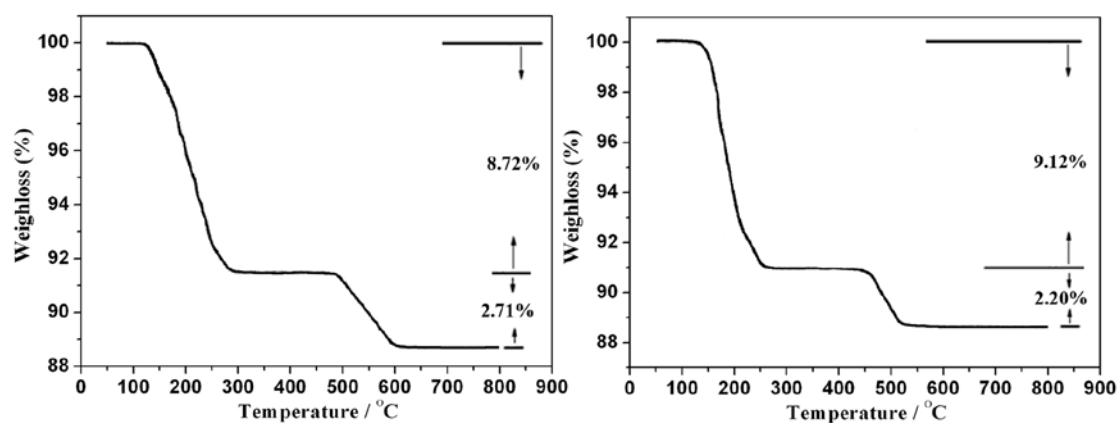


Figure S4. TG curve of compounds **3** (a) and **4** (b).

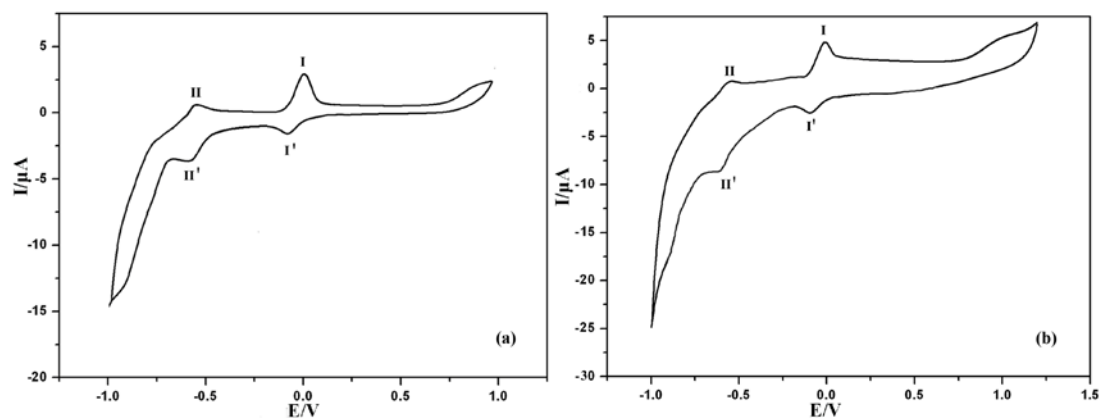


Figure S5. Cyclic voltammograms of compounds **3** (a) and **4** (b).

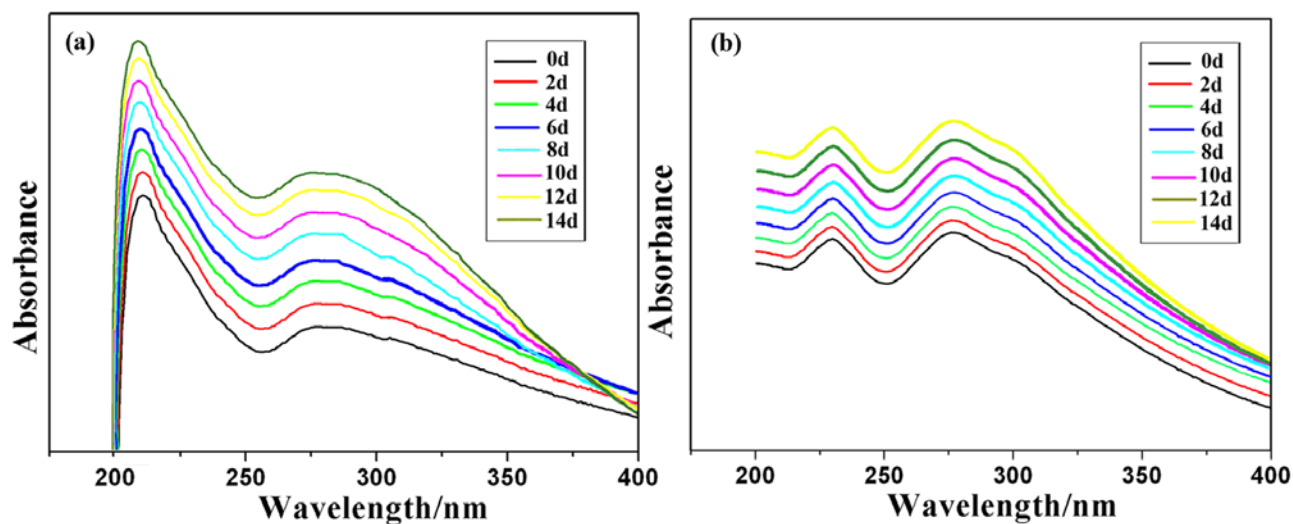


Figure S6. The influence of time on the stability of compounds **3** (a) and **4** (b) in the aqueous solution.

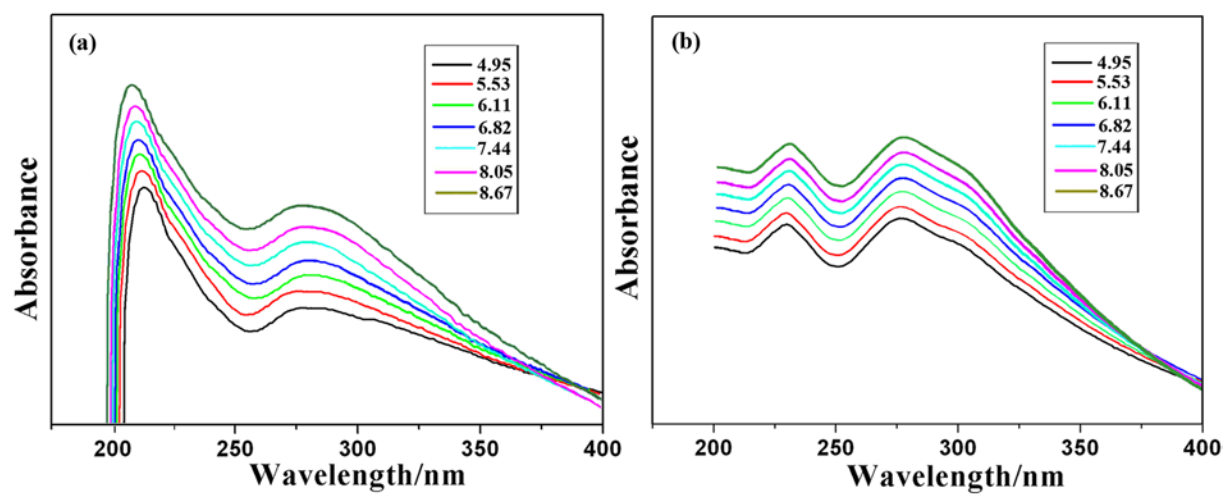


Figure S7. The influence of the pH value on the stability of compounds **3** (a) and **4** (b) in the aqueous solution. pH values of the acidic direction and alkaline direction were adjusted using diluted HCl solution and NaOH solution, respectively.