Electronic Supplementary Material (ESI) for Dalton Transactions.

Controllable assembly, characterization and catalytic property of a new Strandberg-type organophosphotungstate

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1. Crystal structures

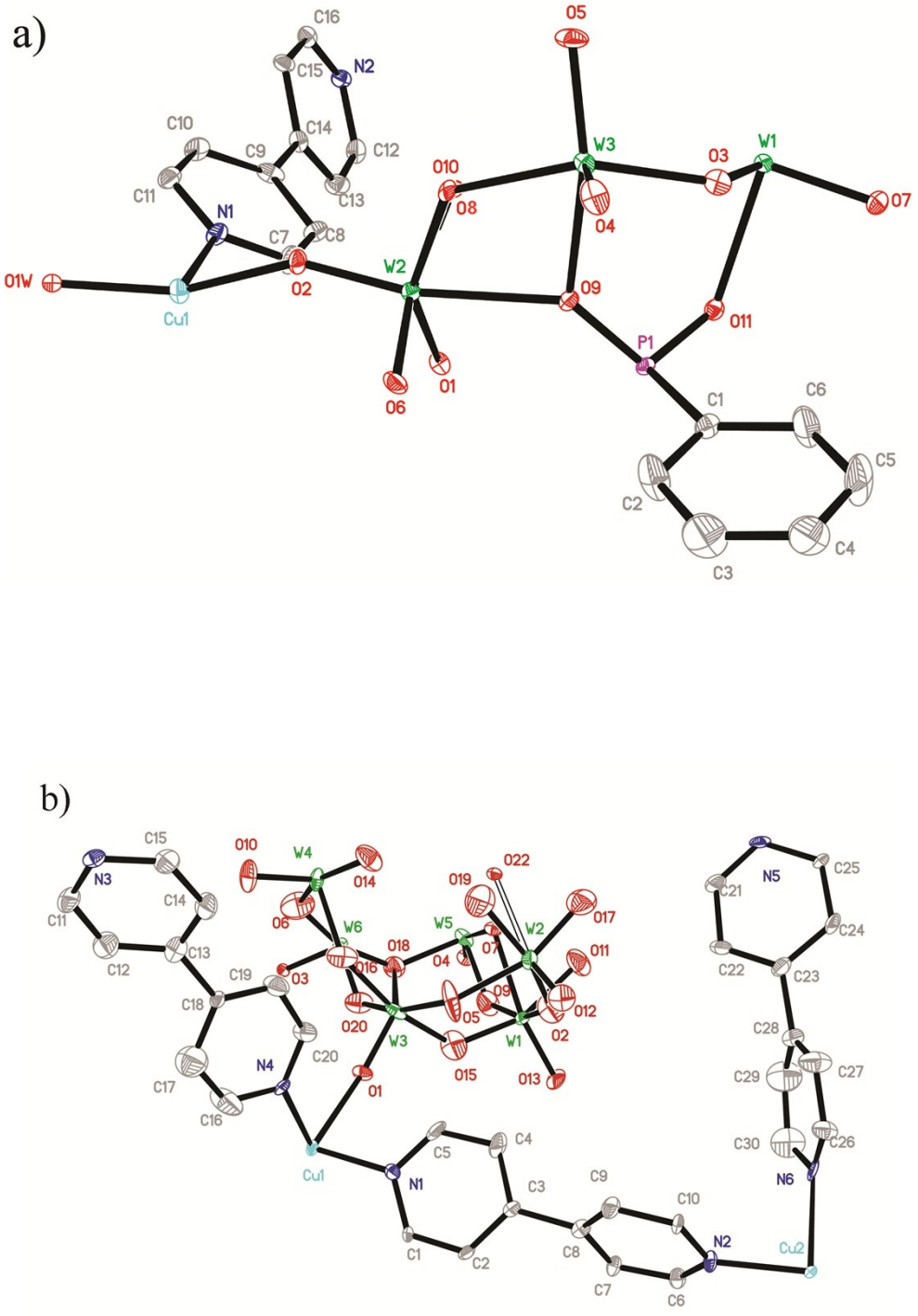


Fig. S1 ORTEP view of the asymmetric units of **1** and **2** (a and b) with atom labeling (30% probability displacement ellipsoids; Hydrogen atoms and free water molecules have been omitted for clarity)

2. Bond lengths and angles

Table S1 Selected bond lengths and angles for compound **1**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1–O7	1.747(9)	W2–O8	1.920 (9)	Cu1–O2	1.961(9)
W1–O7#1	1.747(9)	W2–O10	2.225(8)	Cu1–O1W	1.963(10)
W1–O3#1	1.916(8)	W2–O9	2.314(9)	Cu1–N1	2.008(10)
W1–O3	1.915(8)	W3–O4	1.712(9)	Cu1–N2#2	2.035(10)
W1–O11	2.286(9)	W3–O5	1.736(9)	Cu1–O7#3	2.363(9)
W1–O11#1	2.286(9)	W3–O3	1.922(10)	P1–O10#1	1.499(9)
W2–O6	1.705(9)	W3–O8	1.975(9)	P1–O11	1.534(10)
W2–O2	1.758(9)	W3–O9	2.208(8)	P1–O9	1.579(8)
W2–O1	1.900(3)	W3–O11#1	2.395(8)	P1–C1	1.772(13)
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O7–W1–O7#1	102.2 (6)	O1–W2–O10	79.2(3)	N1–Cu1–O7#3	82.9(4)
O7–W1–O3#1	100.4(4)	O2–W2–O8	101.9(4)	N1–Cu1–N2#2	171.9(4)
O7#1–W1–O3#1	101.4(4)	O4–W3–O3	95.3(4)	O2–Cu1–N1	90.3(4)
O3#1–W1–O3	145.0(6)	O4–W3–O5	103.7(5)	O2–Cu1–O1W	160.8(4)
O3–W1–O11	80.4(3)	O5–W3–O3	104.1(4)	O10#1–P1–O9	108.5(5)
O6–W2–O2	102.5(4)	O3–W3–O8	152.2(3)	O11–P1–O9	110.3(5)
O2–W2–O1	100.4(4)	O3–W3–O9	83.1(3)	O9–P1–C1	108.1(5)
O6–W2–O8	100.2(4)	O1W–Cu1–N2#2	92.8(4)		

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

Table S2 Hydrogen bonds for **1**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (º)
O1W–H1WA...O5#1	0.849(14)	1.89(5)	2.707(13)	161(15)
O1W–H1WB...O8#2	0.849(14)	1.83(3)	2.671(12)	170(15)

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

Table S3 Selected bond lengths and angles for compound **2**

Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
W1–O13	1.71(2)	W3–O20	1.89(3)	W6–O20	1.75(3)
W1–O9	1.90(2)	W3–O21	2.14(3)	W6–O18	1.73(3)
W1–O15	1.82(3)	W3–O8	2.32(4)	W6–O6	2.20(3)
W1–O11	1.92(3)	W4–O10	1.69(2)	W6–O17#1	1.89(3)
W1–O2	1.97(3)	W4–O11#1	1.71(3)	W6–O21	2.21(3)
W1–O7	2.27(3)	W4–O6	1.99(3)	W6–O22#1	2.26(3)
W1–O8	2.27(4)	W4–O16	1.86(3)	Cu1–N1#2	2.02(2)
W2–O12	1.66(2)	W4–O14	1.97(2)	Cu1–N1	2.02(2)
W2–O17	1.74(3)	W4–O21	2.35(3)	Cu1–N4#2	2.15(2)
W2–O2	1.88(3)	W4–O7#1	2.45(3)	Cu1–N4	2.15(2)
W2–O19	1.90(3)	W5–O4	1.691(17)	Cu1–O1	2.308(17)
W2–O5	1.96(2)	W5–O19#1	1.72(3)	Cu1–O1#2	2.308(17)
W2–O22	2.30(3)	W5–O14#1	1.84(2)	Cu2–N3#3	2.04(2)
W2–O8	2.39(3)	W5–O9	1.93(2)	Cu2–N2	2.05(2)
W3–O1	1.697(17)	W5–O18	1.93(3)	Cu2–N5#4	2.08(2)
W3–O5	1.84(2)	W5–O22#1	2.19(3)	Cu2–N6	2.09(2)
W3–O16	1.76(3)	W5–O7	2.29(3)	Cu2–O3#5	2.446(16)
W3–O15	1.84(3)	W6–O3	1.719(15)	Cu2–O4#6	2.478(17)
Bond	Angle (º)	Bond	Angle (º)	Bond	Angle (º)
O13–W1–O9	102.1(13)	O16–W3–O15	144.1(14)	O20–W6–O6	94.7(15)
O13–W1–O15	110.8(14)	O10–W4–O6	88.4(13)	O18–W6–O6	163.1(15)
O9–W1–O15	87.0(13)	O6–W4–O16	92.5(14)	N4#2–Cu1–N4	180.0(12)
O13–W1–O11	111.8(14)	O10–W4–O14	99.4(11)	N1#2–Cu1–O1	90.1(8)
O9–W1–O11	90.1(12)	O6–W4–O14	168.0(13)	N1–Cu1–O1	89.9(8)
O12–W2–O17	114.6(13)	O16–W4–O14	76.3(13)	N1–Cu1–O1#2	90.1(8)
O12–W2–O2	99.3(12)	O4–W5–O19#1	107.6(13)	O1–Cu1–O1#2	180.0(4)
O17–W2–O2	90.9(13)	O4–W5–O14#1	99.2(10)	N3#3–Cu2–N2	177.2(9)
O12–W2–O19	111.1(14)	O4–W5–O18	108.0(13)	N2–Cu2–N5#4	91.9(9)
O17–W2–O19	87.7(14)	O4–W5–O9	100.6(10)	N2–Cu2–O4#6	91.0(7)
O1–W3–O16	105.8(11)	O19#1–W5–O9	151.6(15)	N6–Cu2–O4#6	85.1(8)
O5–W3–O16	87.9(14)	O3–W6–O20	112.4(13)	O3#5–Cu2–O4#6	177.1(6)
O1–W3–O15	109.8(13)	O20–W6–O18	75.8(18)		
O5–W3–O15	91.6(12)	O3–W6–O6	85.7(10)		

Symmetry transformations used to generate equivalent atoms: #1 -x-1, -y, -z+2; #2 -x, -y, -z+3; #3 x+1, -y+1/2, z-1/2; #4 x+1, -y+1/2, z+1/2; #5 -x, y+1/2, -z+5/2; #6 -x, -y, -z+2

3. Characterizations

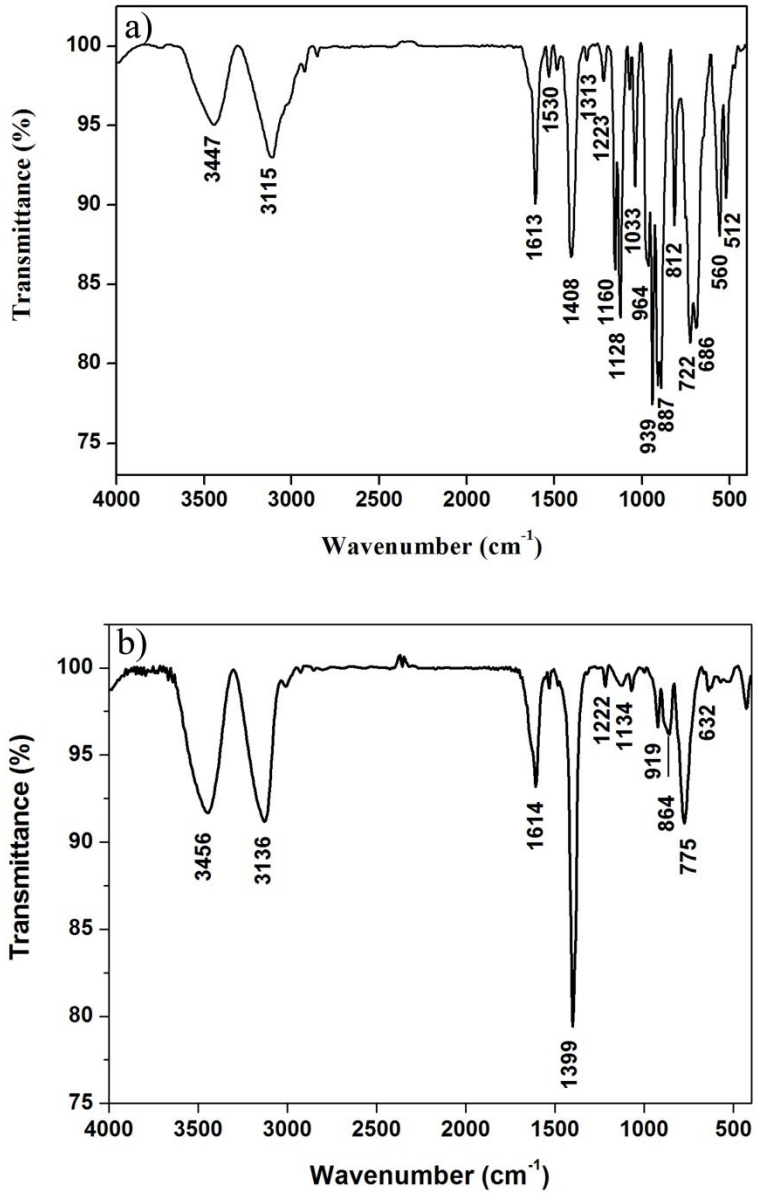


Fig. S2 IR spectra of **1** and **2** (a and b)

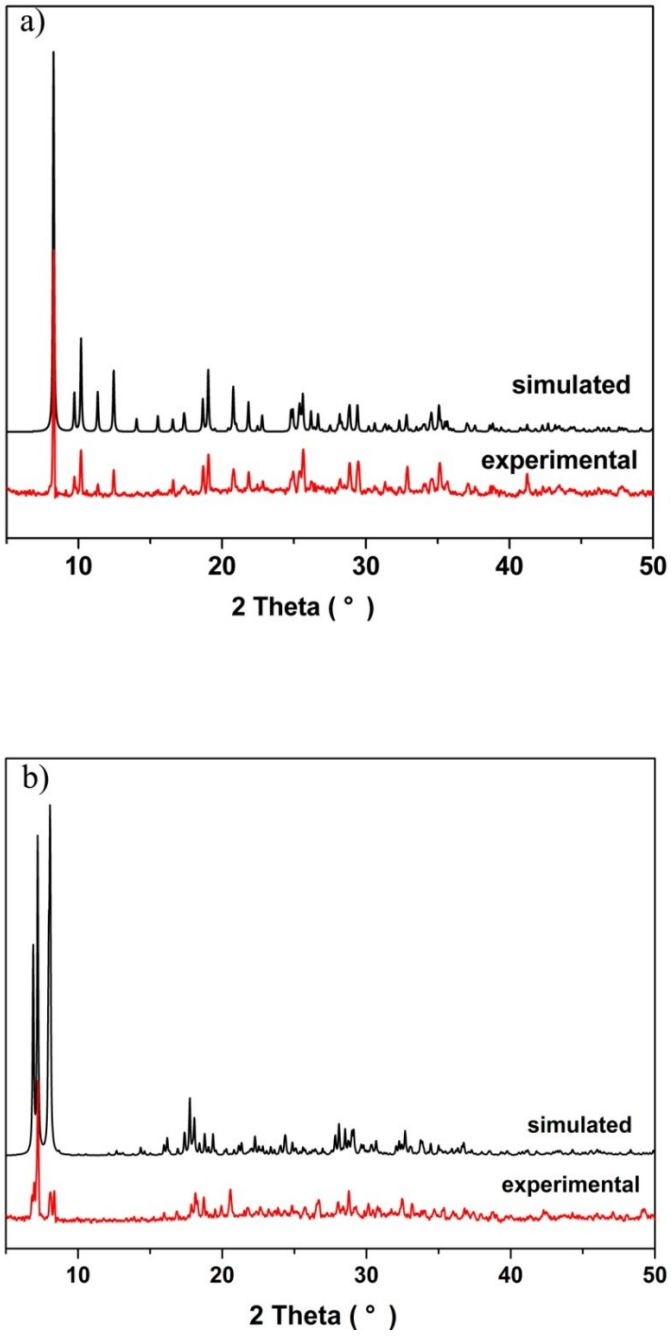


Fig. S3 The simulated and experimental XRPD patterns of **1** and **2** (a and b)

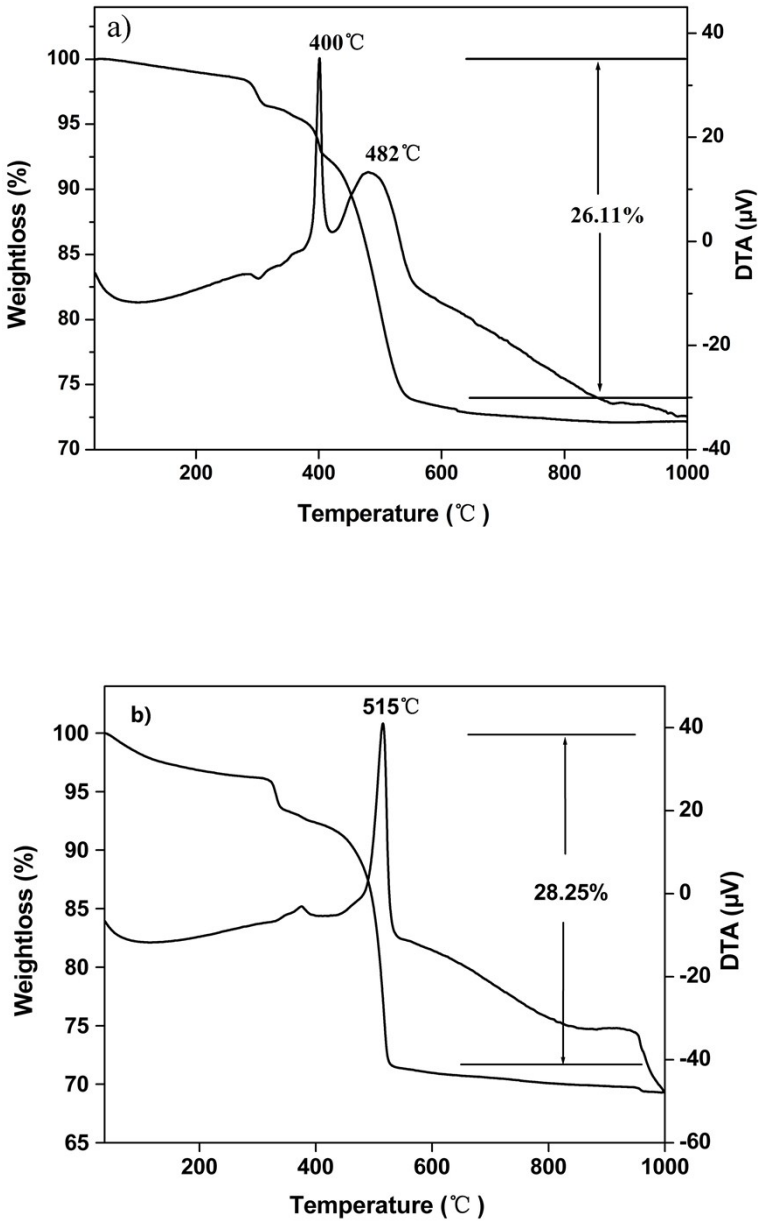


Fig. S4 The TG-DTA curves of **1** and **2** (a and b)

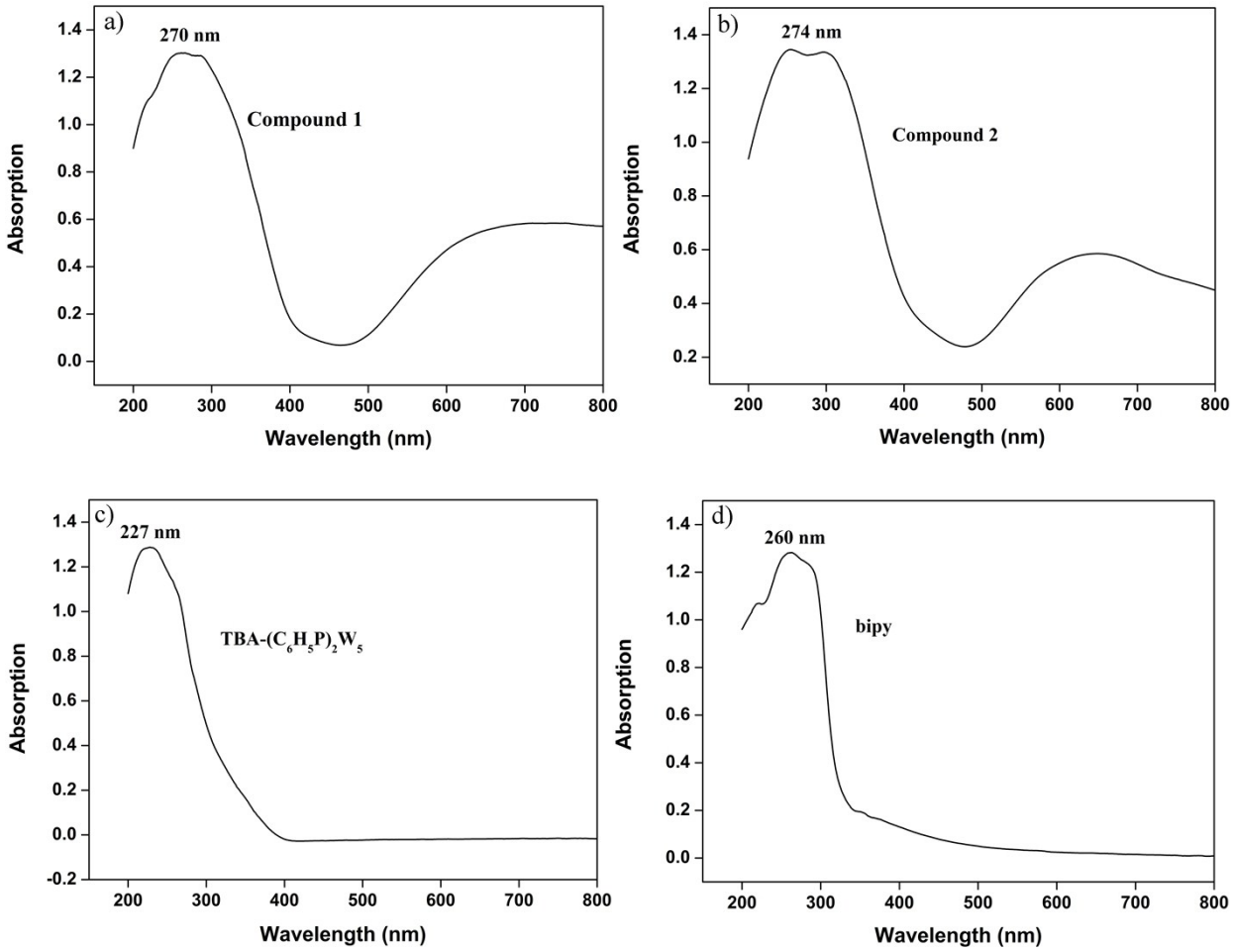


Fig. S5 Solid UV-vis absorption spectra of the compound **1** (a), **2** (b), the parent compound TBA-$(C_6H_5P)_2W_5$ (c), and bipy (d) at room temperature

4. Fluorescence properties and catalytic activity tests

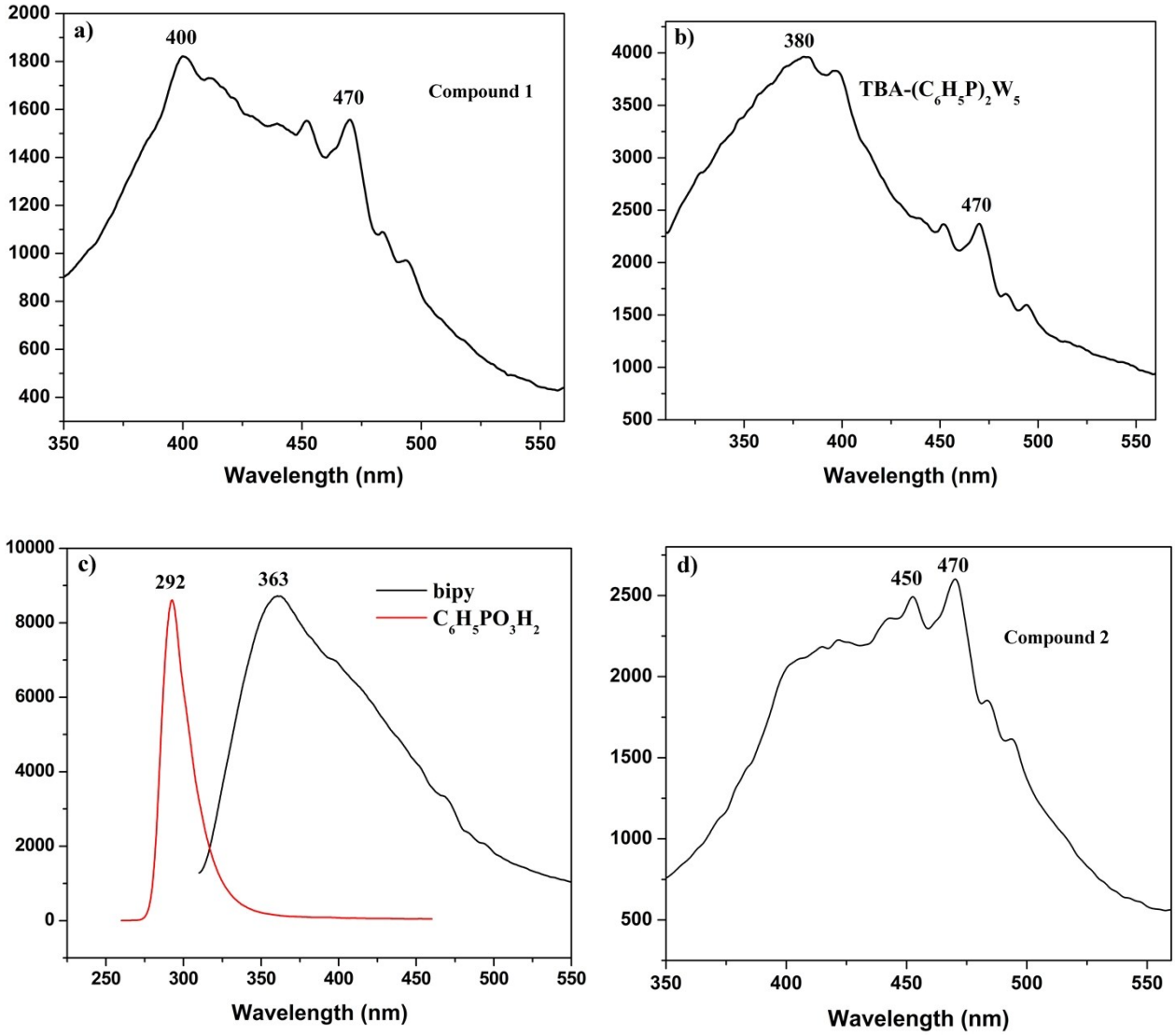
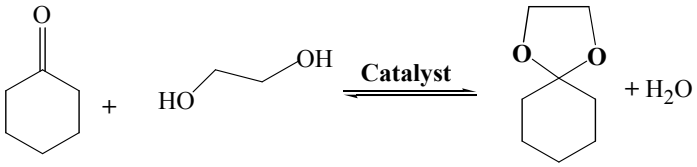


Fig. S6 Solid state emission spectra of the compound **1** (a), **2** (d), the parent compound TBA-$(C_6H_5P)_2W_5$ (b), bipy and phenylphosphonic acid ($C_6H_5PO_3H_2$) (c) at room temperature



Scheme S1 Ketalization of cyclohexanone with glycol

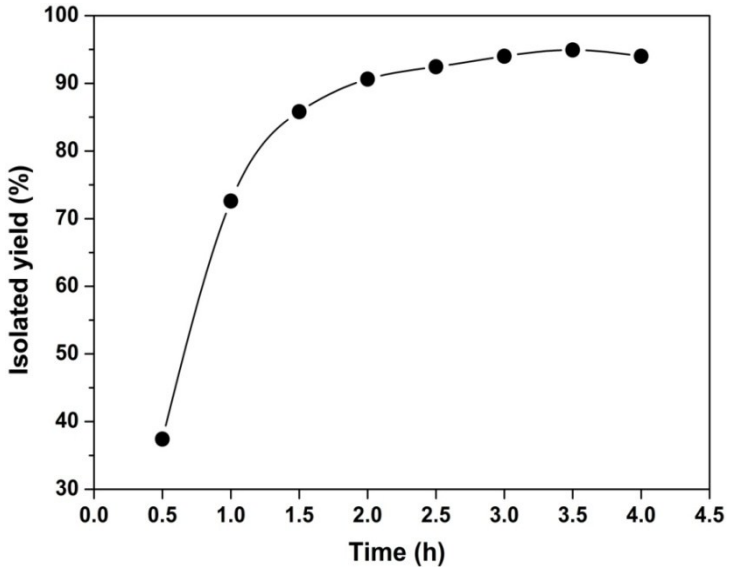


Fig. S7 Effect of reaction time on cyclohexanone ethylene ketal yield: cyclohexanone (0.1 mol)/glycol molar ratio, 1: 1.4; catalyst (based on W)/cyclohexanone molar ratio, 1: 350; reaction temperature, 95-100 °C; water-carring agent, cyclohexane (10 mL)

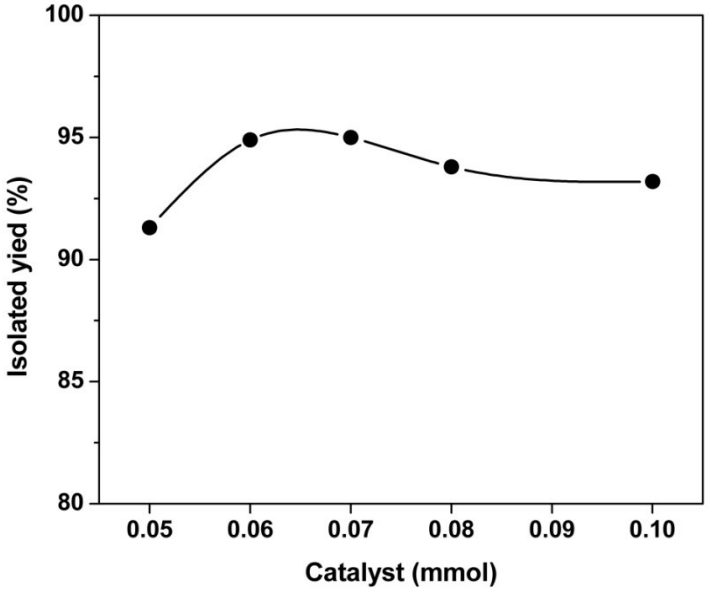


Fig. S8 Effect of the amount of **1** on cyclohexanone ethylene ketal yield: cyclohexanone (0.1 mol)/glycol molar ratio, 1: 1.4; reaction temperature, 95-100 °C; reaction time, 3.5 h; water-carring agent, cyclohexane (10 mL)

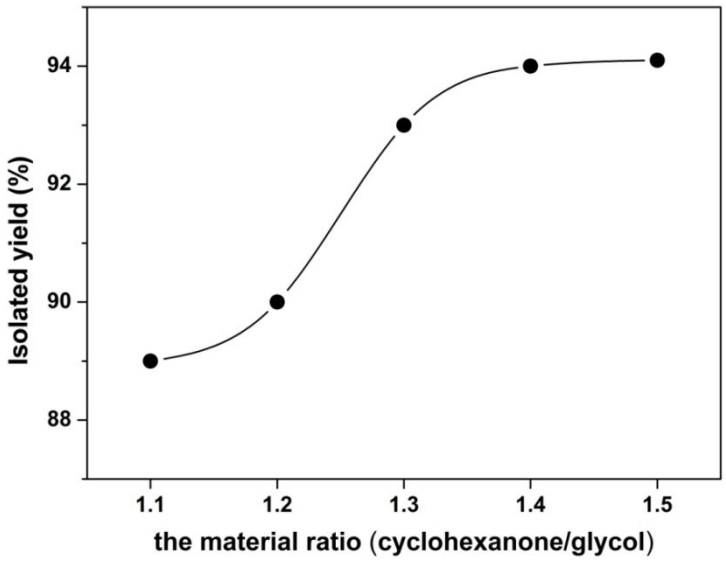


Fig. S9 Effect of the material ratio on cyclohexanone ethylene ketal yield: catalyst (based on W)/cyclohexanone (0.1 mol) molar ratio, 1: 350; reaction temperature, 95-100 °C; reaction time, 3.5 h. water-carring agent, cyclohexane (10 mL)