Table s1. BVS calculation results of tungsten atoms in compound 1.

Atom	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	Sum
BVS value	6.01	5.96	5.99	5.92	6.01	6.07	5.99	5.94	6.03	6.03	6.08	5.97	72.0

The equation used is "Bond valence = $10^{(-0.5\times(R-R_0)/R)}$", and R_o= 1.91.

Table s2. BVS calculation results of tungsten atoms in compound 2

Atom	W1	W2	W3	W4	W5	W6	Sum
BVS value	6.03	5.96	5.95	5.99	5.93	6.02	35.9

The equation used is "Bond valence = $10^{(-0.5*(R-R_0)/R)}$", and R_o= 1.91.

Synthesis discussion:

1. For compound **1**:

The same procedure with $AgNO_3$ (0.134g, 0.789mmol) used in place of $AgNO_3$ (0.101g, 0.595mmol) has been done, and we only obtained some crystals unsuitable for crystal analysis. The same procedure with Hbzmd (0.033g, 0.094mmol) instead of Hbzmd (0.05g, 0.142mmol) has been done, and we only obtained some unidentified amorphous materials.

The same procedure with both $H_4[SiW_{12}O_{40}]\cdot xH_2O$ (0.496g, 0.172mmol) and isonicotinic acid (0.10g, 0.812mmol) replacing $H_4[SiW_{12}O_{40}]\cdot xH_2O$ (0.5g, 0.174mmol) and isonicotinic acid (0.107g, 0.869mmol) hse been done, and we also only obtained some crystals unsuitable for crystal analysis.

2. For compound **2**:

The same procedure with only $H_3[PW_{12}O_{40}]\cdot xH_2O$ (0.33g, 0.115mmol) taking the place of $H_3[PW_{12}O_{40}]\cdot xH_2O$ (0.5g, 0.174mmol) has been carried out, and we only obtained some crystals unsuitable for crystal analysis. The same procedure with both isonicotinic acid (0.12g, 0.975mmol) and Hbzmd (0.05g, 0.142mmol) replaced by isonicotinic acid (0.107g, 0.869mmol) and Hbzmd (0.033g, 0.093mmol) and with both $H_3[PW_{12}O_{40}]\cdot xH_2O$ (0.5g, 0.174mmol) and isonicotinic acid (0.12g, 0.975mmol) replaced by $H_3[PW_{12}O_{40}]\cdot xH_2O$ (0.33g, 0.115mmol) and isonicotinic acid (0.10g, 0.812mmol) have also been done, and we only obtained some unidentified amorphous materials.

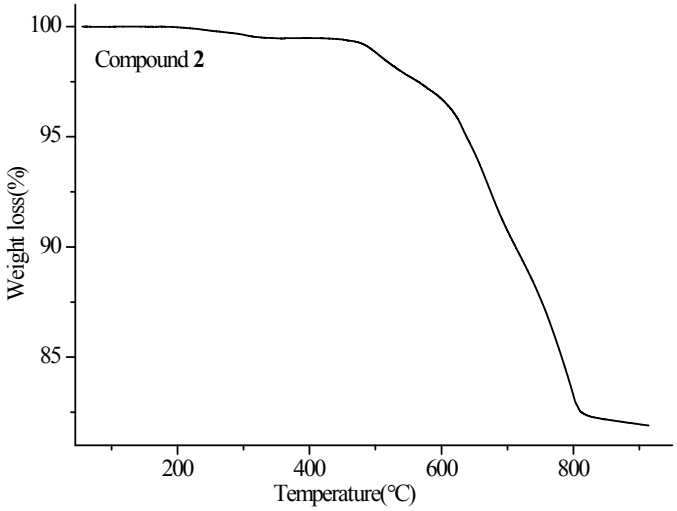


Fig. s1 TG curve for compound **2**.

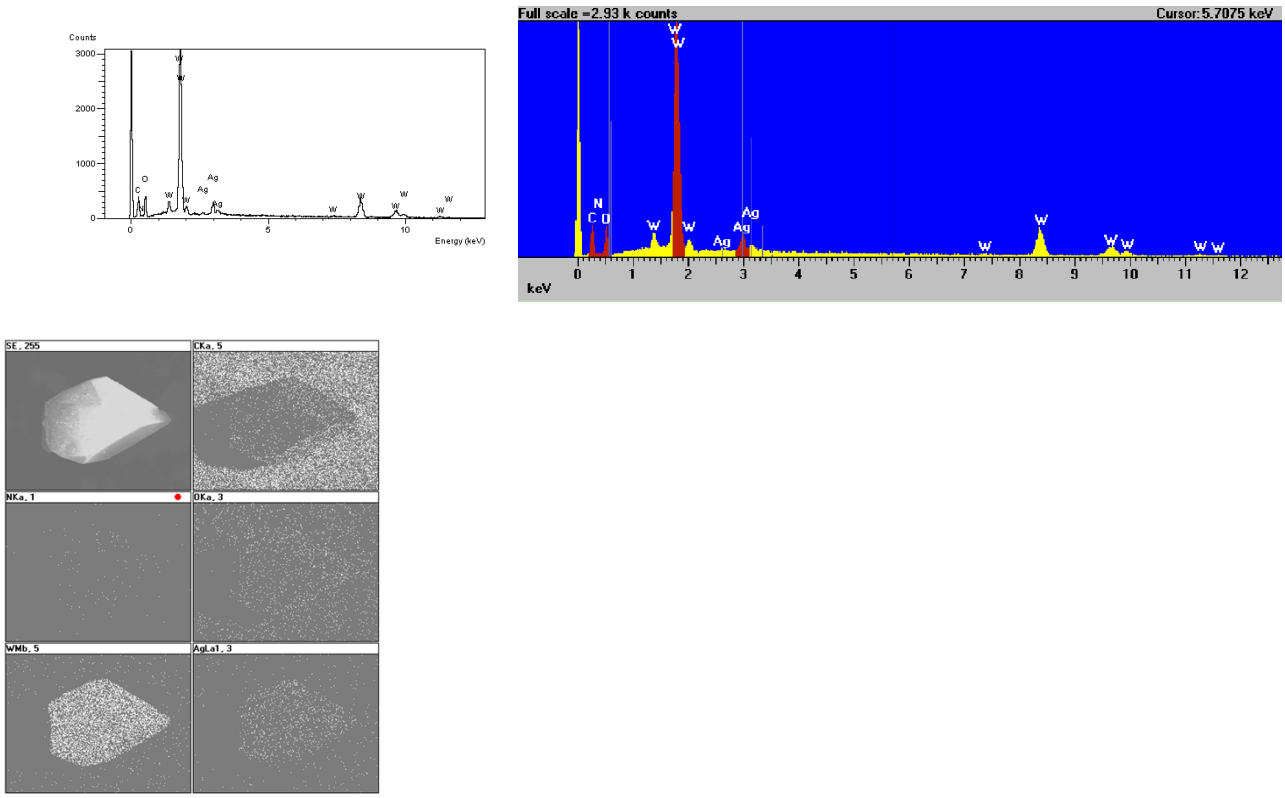


Fig. s2 EDS spectrum for compound **2**.

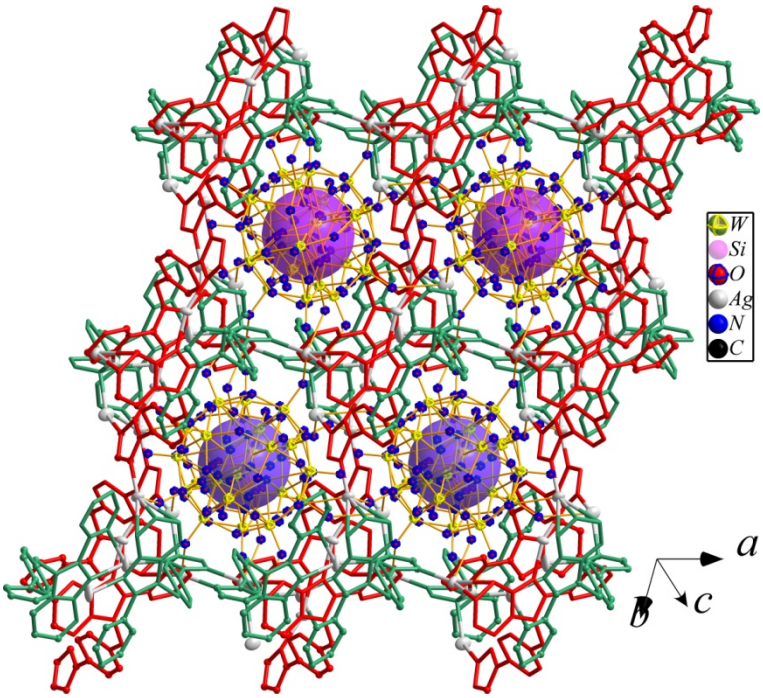


Fig. s3 representation of the 3-D POMMOF in compound **1**. N(1) bzmd is in red, and N(8) bzmd is in green, Si(1) centered POM are in pink, and Si(2) centered POM are in blue.

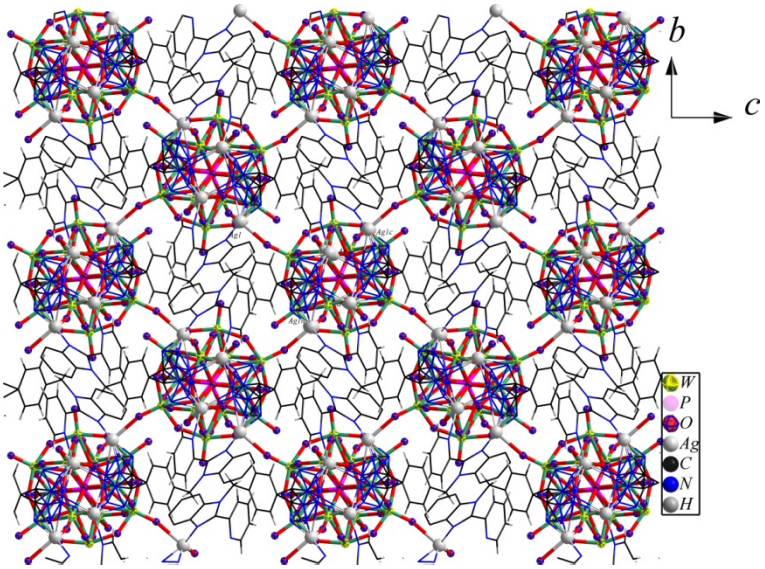


Fig. s4 representation of the 3-D POMMOF in compound **2**.

Characterizations of compounds.

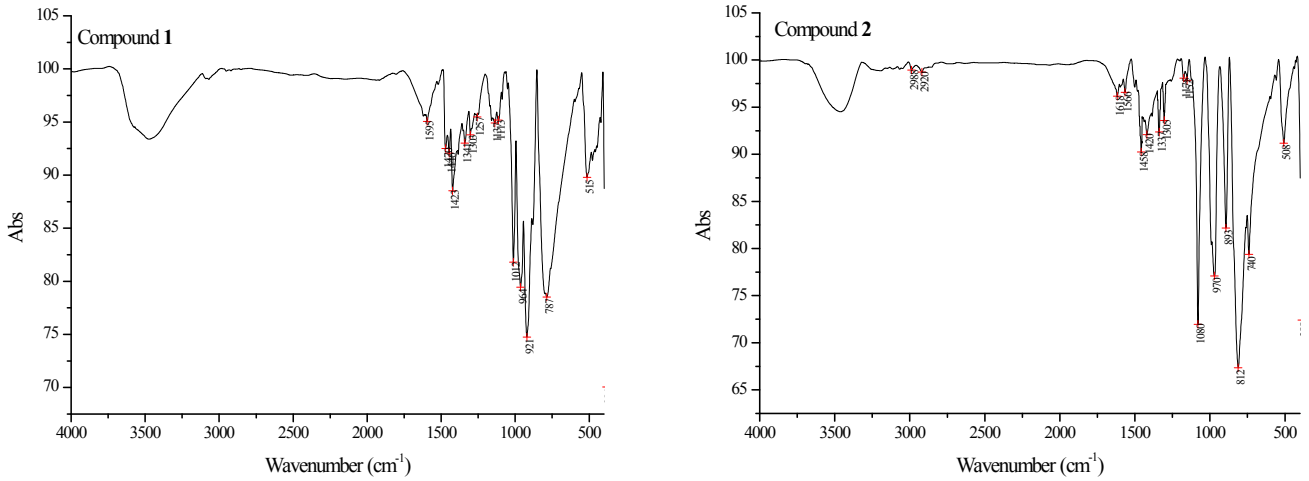


Fig. s5 IR spectra of compounds **1** and **2**.

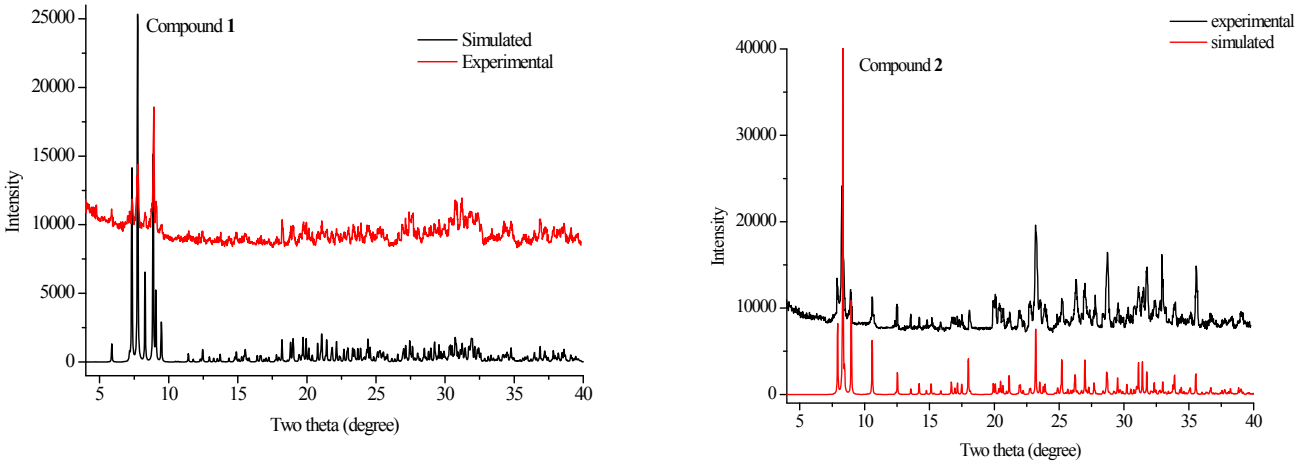


Fig. s6 experimental and simulated XRD patterns of compounds **1** and **2**.

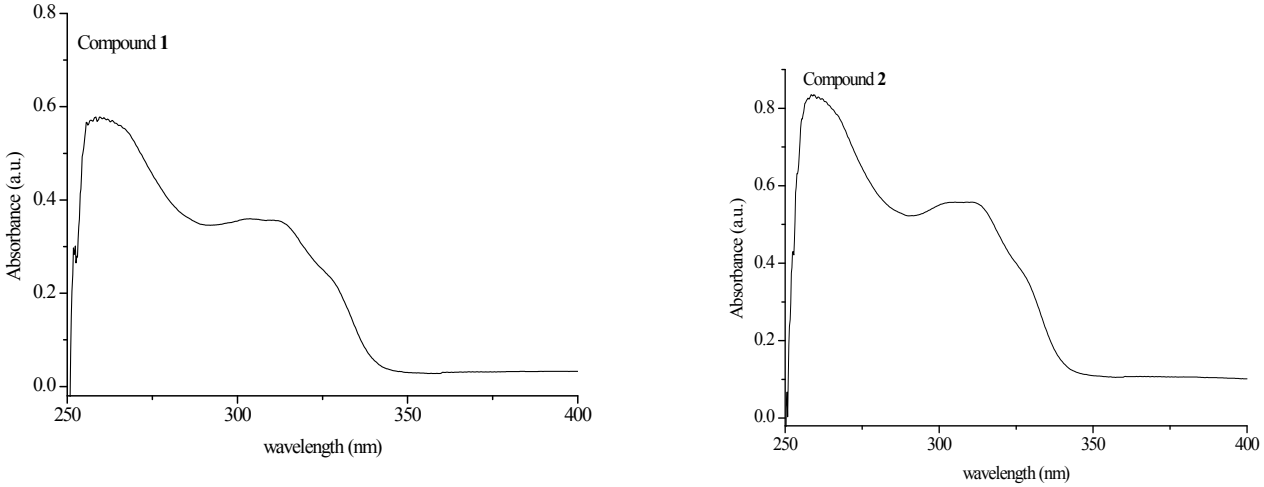


Fig. s7. UV spectra of compounds **1** and **2**.

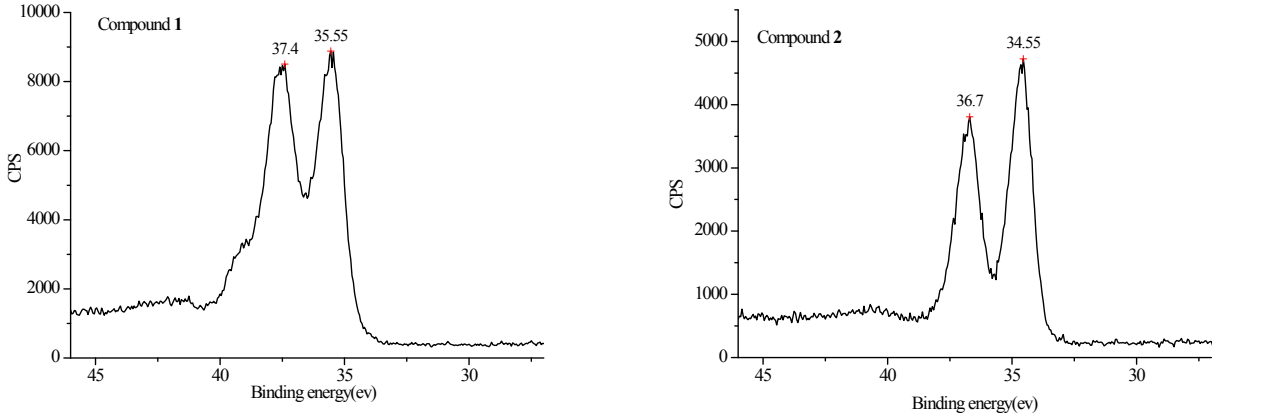


Fig. s8 XPS spectra of compound **1** (a) and compound **2** (b).

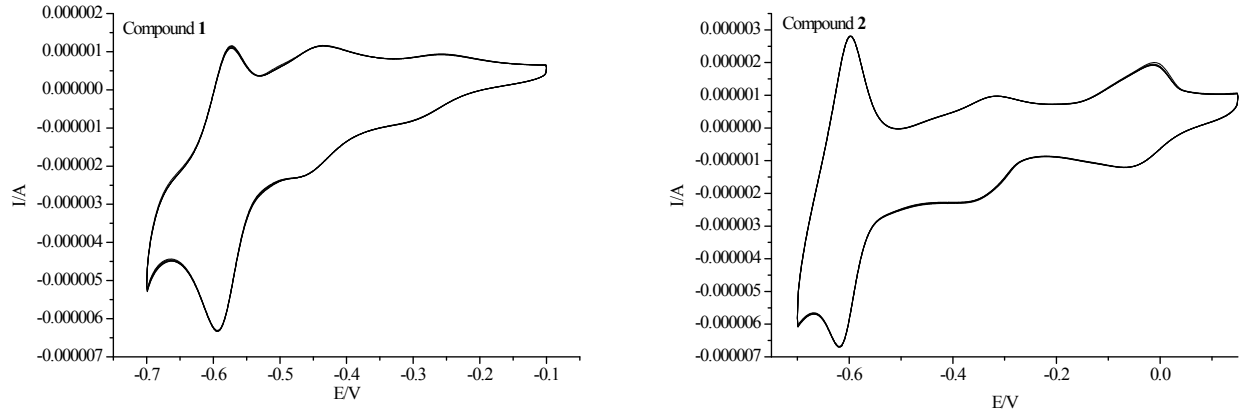
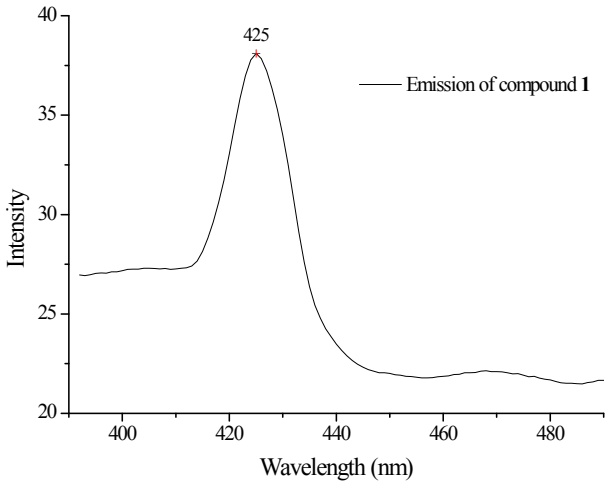
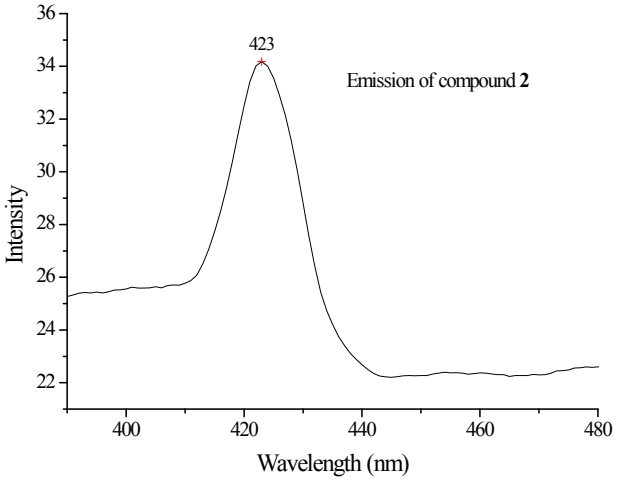


Fig. s9 cyclic voltammograms of compounds **1** and **2**.





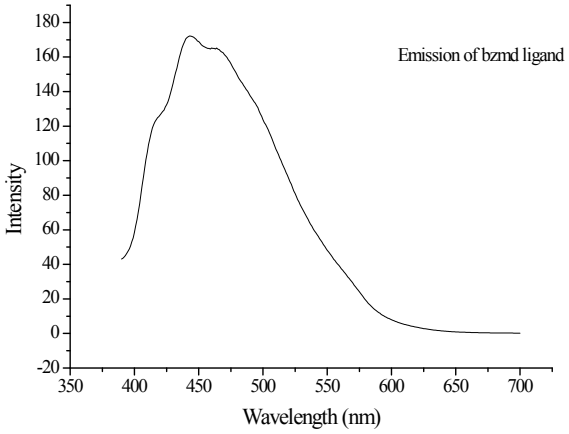


Fig. s10 The photoluminescence properties of compounds **1** and **2**.

References:

1. S. Q. Liu, Z. Shi, S. J. Dong, *Electroanalysis* 1998**, 10** (13), 891-896.