Supplementary experimental information

The synthesis method of phosphomolybdic acid: Dissolve 20 g sodium molybdate in 40 mL water, add 2 mL 85% phosphoric acid, add 20 mL concentrated hydrochloric acid drop by drop, transfer the yellow transparent mixture to a separatory funnel, add 30 mL ether extraction, cool until stratification occurs, transfer the bottom layer to the separatory funnel, add 20 mL water, shake and add 10 mL concentrated hydrochloric acid to Ph 1.5~5, then add 20 mL ether extraction, cool and keep the ether layer for drying and recrystallization operation to obtain the target compound.

The synthesis method of silicomolybdic acid: mix 37 mL of 13 M concentrated nitric acid with 120 mL of 1 M sodium molybdate solution, then add 50 mL of 0.2 M sodium silicate solution drop by drop until the solution turns yellow, put the reaction at 80℃ for 30 min, then add 48 mL of 12 M concentrated hydrochloric acid for acidification to pH 3.8~4.8, extract with ether, keep the ether layer for drying and recrystallization to get the target compound. The target compound was obtained by drying and recrystallization.

The synthesis method of gallium-molybdate: dissolve 5.5g 22.7mM sodium molybdate in 1.5 mL ultrapure water, mix well with 2.5 mL 60% nitric acid, then add 0.721 g 1.8 mM gallium nitrate. The mixed solution was heated at 90℃ and pH 1.5 for 1h, and after the solution turned yellow, an appropriate amount of 12 M concentrated hydrochloric acid was added and extracted with ether, and the ether layer was retained for drying and recrystallization operation to obtain the target compound.

Full wavelength scans were performed using FTIR (scan range 400-4000 cm^{-1}) and UV-Vis spectrophotometer (scan range 190-800 nm), and the data obtained were plotted and analyzed, and compared with phosphomolybdic acid, silicomolybdic acid, and gallium molybdic acid in the literature. The results showed that all three compounds exhibited characteristic bands of Keggin-type structures, in agreement with Refs.[1]-[3]

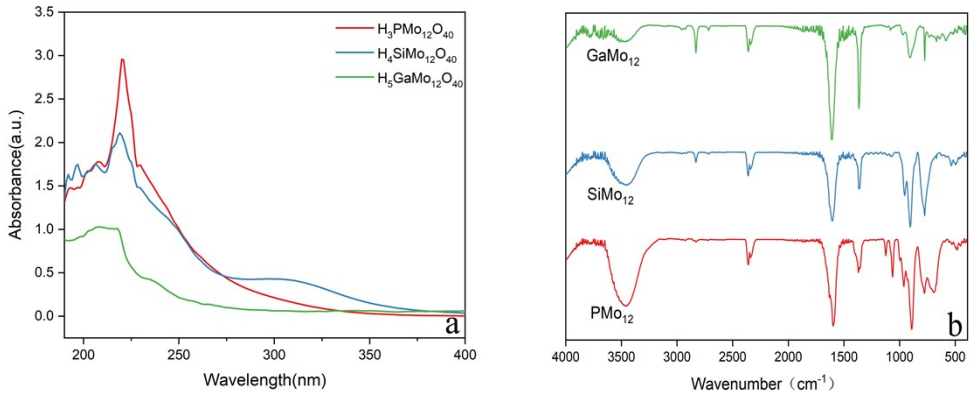

Figure 1 a. UV-Vis spectra of PMo_{12}、$SiMo_{12}$ and $GaMo_{12}$; b. IR spectra of PMo_{12}、$SiMo_{12}$ and $GaMo_{12}$

Specific synthesis technique for $PMo_{11}Fe$, $PMo_{11}Cu$, and $PMo_{11}Mn$: $FeCl_3$ ($CuCl_2$, $MnCl_2$), Na_2MoO_4, and 1.72 mL (85%) of H_3PO_4 were dissolved in 400 mL of ultrapure water, heated to reflux for 7 hours, cooled to room temperature, and 75 mL of concentrated sulfuric acid were added. The target compound can then be obtained by adding 75 mL of strong hydrochloric acid to acidify the mixture, followed by the required amount of anhydrous ether to extract it. The ether layer solution is then collected for drying and recrystallization.

Full wavelength scans were performed using FTIR (scan range 400-4000 cm^{-1}) and UV-Vis spectrophotometer (scan range 190-800 nm), and the data obtained were plotted and analyzed, and compared with phosphomolybdic acid, silicomolybdic acid, and gallium molybdic acid in the literature. The results showed that all three compounds exhibited characteristic bands of Keggin-type structures, in agreement with Refs.[4],[5]

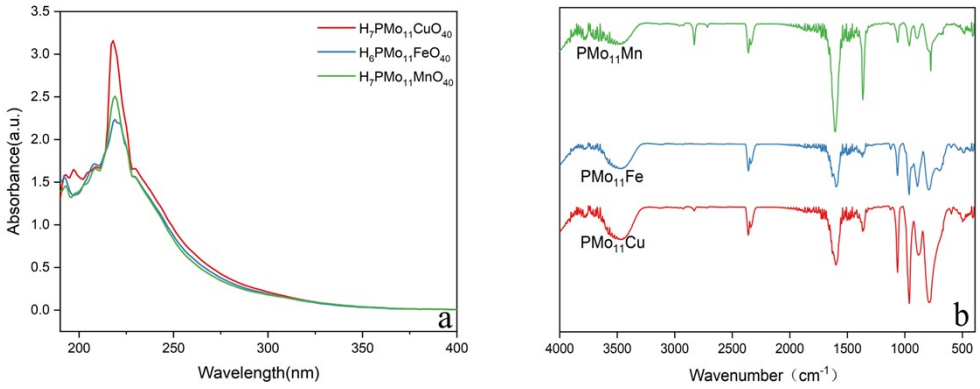

Fig.2 a. UV-Vis spectra of $PMo_{11}Cu$、$PMo_{11}Fe$ and $PMo_{11}Mn$; b.IR spectra of $PMo_{11}Cu$、$PMo_{11}Fe$ and $PMo_{11}Mn$

Keggin-type polyoxometalate $H_{3+n}PMo_{12-n}V_nO_{40}$ with different numbers of vanadium substitutions (n=1,2,3,4,5) specific synthesis method: According to the molar ratio Na_2HPO_4: Na_2MoO_4: $NaVO_3$= (1:11:1, 1:10:2, 1:9:3, 1:8:4, 1:7:5) weigh the above reagents and dissolve in 400mL ultrapure water. Then add 1:1 sulfuric acid to adjust the pH of the mixture to 2.5, heat the mixture at 80°C and reflux for 6h, cool to room temperature, add appropriate amount of anhydrous ether and sulfuric acid extraction, collect the ether layer solution for drying and recrystallization operation to obtain the target compound.

Full wavelength scans were performed using FTIR (scan range 400-4000 cm^{-1}) and UV-Vis spectrophotometer (scan range 190-800 nm), and the data obtained were plotted and analyzed, and compared with phosphomolybdic acid, silicomolybdic acid, and gallium molybdic acid in the literature. The results showed that all three compounds exhibited characteristic bands of Keggin-type structures, in agreement with Refs.[6]

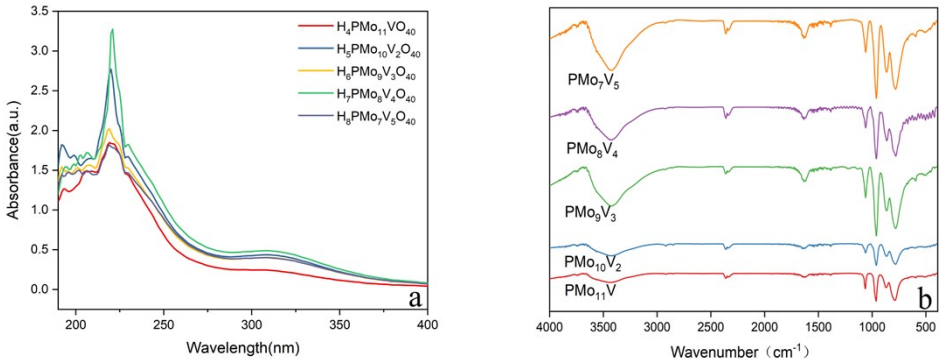

Fig.3 a. UV-Vis spectra of compounds; b. IR spectra of compounds

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