

Electronic Supplementary Information

Unusual visible luminescence of aluminum polyoxocations in aqueous solution

Zhaosheng Qian,^{*,‡} Congcong Chen,[‡] Jianrong Chen, Lichun Kong, Chen Wang, Jin Zhou and Hui

Feng^{*}

College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, P. R. China

1. **Figure S1.** The ^{27}Al NMR spectra of K-Al_{13} and Al_{30} in aqueous solution
2. **Figure S2.** The ^{71}Ga NMR spectrum of K-GaAl_{12} in aqueous solution
3. **Figure S3.** Ultra-violet absorption spectra of K-MAl_{12} ($\text{M} = \text{Al}, \text{Ga}$ and Ge) and Al_{30} in aqueous solution
4. **The ICP-AES analysis of K-GeAl_{12}**
5. **Experimental details**

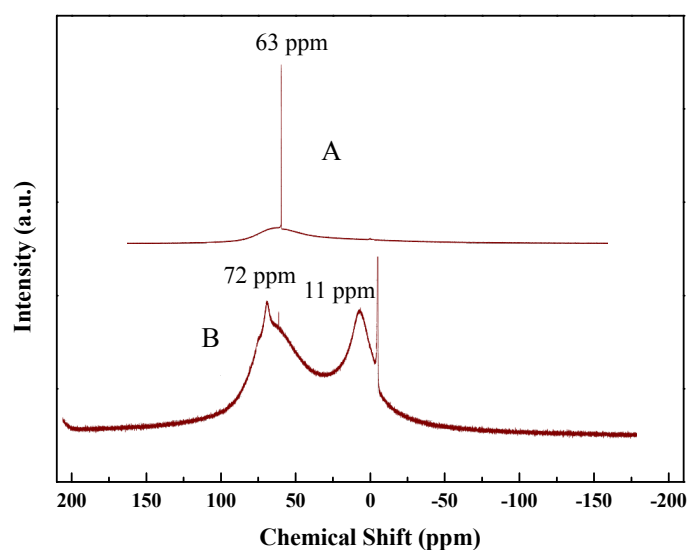


Figure S1. The ^{27}Al NMR spectra of K-Al_{13} (A) and Al_{30} (B) in aqueous solution

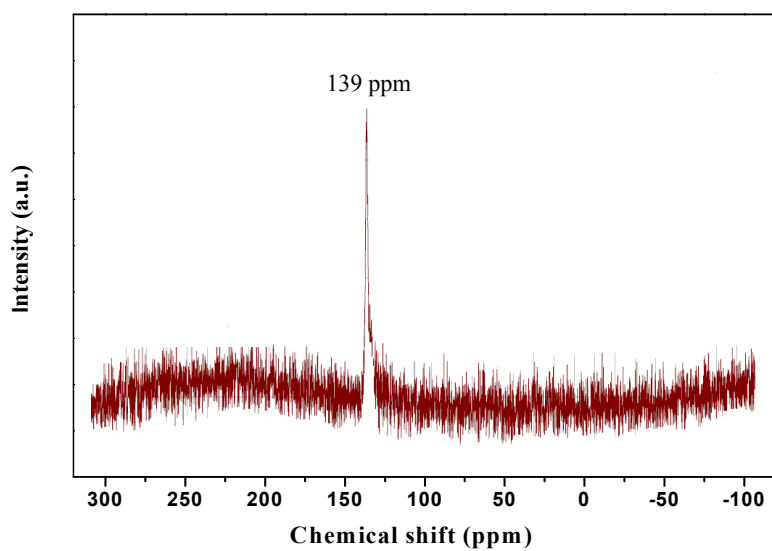


Figure S2. The ^{71}Ga NMR spectrum of K-GaAl_{12} in aqueous solution

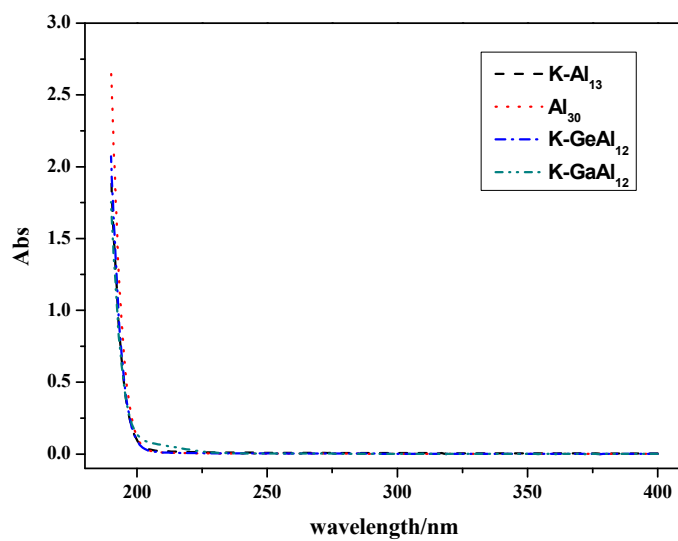


Figure S3. Ultra-violet absorption spectra of K-MAl_{12} ($M = \text{Al, Ga}$ and Ge) and Al_{30} in aqueous solution

4. The ICP-AES analysis of K-GeAl₁₂

In order to confirm the K-GeAl₁₂, the inductively coupled plasma atomic emission spectroscopy of the sample was recorded. The qualitative analysis indicates that the sample includes germanium and aluminum atoms, consistent with components of K-GeAl₁₂. A series of the standard solutions of AlCl₃ and Ge(OH)₂ (GeO₂ was dissolved in NaOH solution) were prepared to produce the calibration curves for aluminum and germanium respectively as shown in the following figures. According to the two calibration curves, the concentrations of Al and Ge in the sample were 6.317 and 0.480 ppm, and the ratio of Ge and Al in the sample is about 13, which is very close to the ratio for K-GeAl₁₂. The small error may be induced by the small amount of K-Al₁₃ included in the sample.

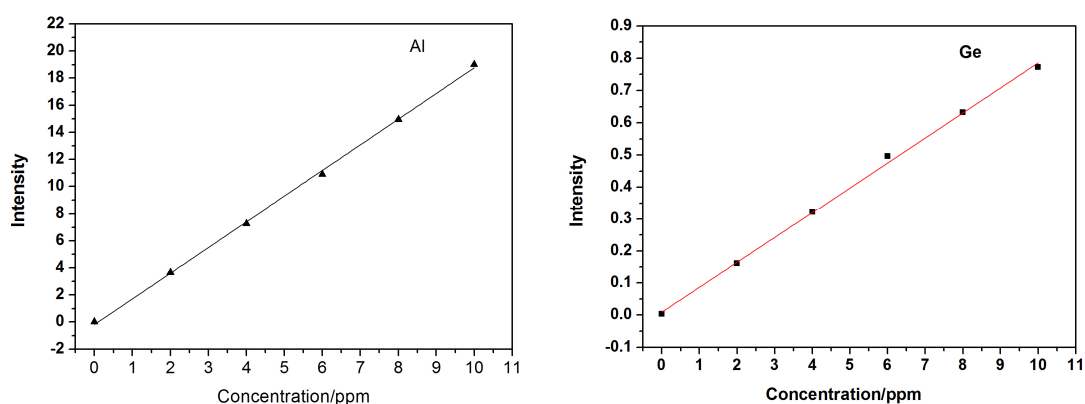


Figure S4. The calibration curves of AlCl₃ (left) and GeO₂ (right)

5. Experimental details

Preparation of sulfate salts of K-Al₁₃, K-GaAl₁₂, K-GeAl₁₂ and Al₃₀. For K-Al₁₃: 110 ml of NaOH solution (0.25 mol L⁻¹) was added dropwise to 50 ml of AlCl₃ solution (0.25 mol L⁻¹) maintained at 80 °C under fast stirring, and the resulting solution was aged for 24 hours. Finally, the crystalline salts Na[AlO₄Al₁₂(OH)₂₄(H₂O)₁₂](SO₄)₄·10H₂O was obtain by adding 125 ml of Na₂SO₄ solution (0.1 mol L⁻¹) to the aged solution. For K-GaAl₁₂: 110 ml of NaOH solution (0.25 mol L⁻¹) was added dropwise to the mixed Al³⁺ and Ga³⁺ solutions in a 12:1 mole ratio maintained at 95 °C, and then 125 ml of Na₂SO₄ solution (0.1 mol L⁻¹) was added to the resulting K-GaAl₁₂ solution to obtain the crystalline salts Na[GaO₄Al₁₂(OH)₂₄(H₂O)₁₂](SO₄)₄·10H₂O. For K-GeAl₁₂: 110 ml of NaOH solution (0.25 mol L⁻¹) containing 0.1308 g GeO₂ was added dropwise to 50 ml of AlCl₃ solution (0.25 mol L⁻¹) maintained at 95 °C, in which the [Ge]:[Al] mole ratio is 1:10, and then 125 ml of Na₂SO₄ solution (0.1 mol L⁻¹) was added to the resulting K-GeAl₁₂ solution to obtain the crystalline salts

$[\text{GeO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$. For Al_{30} : NaOH solution (2 mol L^{-1}) was added dropwise to an AlCl_3 solution (0.3 mol L^{-1}) maintained at $95 \text{ }^\circ\text{C}$ under fast stirring, in which the hydrolysis ratio was 2.46. The resulting solution was further heated and stirring over 48 hours at $95 \text{ }^\circ\text{C}$. Crystallization was induced by addition of Na_2SO_4 to the obtained solution with the $[\text{SO}_4]:[\text{Al}]$ ratio of 0.33.

Preparation of pure K- Al_{13} , K- GaAl_{12} , K- GeAl_{12} and Al_{30} solutions. Crystalline sulfate salts of K- Al_{13} , K- GaAl_{12} , K- GeAl_{12} and Al_{30} were synthesized according to the above procedures. Cluster solutions were obtained by BaSO_4 metathesis using BaCl_2 . For example, the $\text{Na}[\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_4 \cdot 10\text{H}_2\text{O}$ was added to 20 ml of water to pre-disperse the solid, and then the identical amount of BaCl_2 solution was added. The resulting mixture was treated under ultrasonication for 4 hours, centrifuged, and then filtered by $0.1 \text{ }\mu\text{m}$ membrane.

Determination of the quantum yields. Determination of the quantum yields of these aluminum polyoxocations was accomplished by comparison of the wavelength integrated intensity of these aluminum polyoxocations to that of the standard quinine sulfate. The optical density is kept below 0.05 to avoid inner filter effects. The quantum yields of these aluminum polyoxocations were calculated using

$$\Phi = \Phi_S [(I \cdot A_S)/(I_S \cdot A)]$$

Where Φ is the quantum yield, I is the integrated intensity, A is the optical density. The subscript S refers to the standard reference of known quantum yield. In this work, quinine sulfate was chosen as the standard, whose quantum yield is 0.577.

Preparation of the solutions with additional ions. Since the K- Al_{13} is stable at pH 4.6, all the chosen ions solutions were adjusted to pH 4.6 to avoid the decomposition of K- Al_{13} . The resulting ions solutions were added to the same amount of K- Al_{13} solutions respectively to obtain the series of mixed solutions, in which the concentration of K- Al_{13} is about $6.0 \times 10^{-3} \text{ mol L}^{-1}$, and the concentration of the ions are about 1.0×10^{-3} , 1.0×10^{-2} and $5.0 \times 10^{-2} \text{ mol L}^{-1}$ respectively. In all the mixed solutions, the concentration of K- Al_{13} was identical to raw solution with pure K- Al_{13} .