

**Supporting information of**

# Study of aqueous Am(III)-aliphatic dicarboxylate complexes: Coordination mode-dependent optical property and stability changes

*Hee-Kyung Kim,<sup>1\*‡</sup> Keunhong Jeong,<sup>2‡</sup> Hye-Ryun Cho,<sup>1</sup> Kyungwon Kwak,<sup>3,4\*</sup> Euo*

*Chang Jung,<sup>1</sup> Wansik Cha<sup>1</sup>*

<sup>1</sup> Nuclear Chemistry Research Team, Korea Atomic Energy Research Institute,

Daejeon 34057, Republic of Korea

<sup>2</sup> Department of Chemistry, Korea Military Academy, Seoul 01805, Republic of Korea

<sup>3</sup> Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS),

Korea University, Seoul 02841, Korea.

<sup>4</sup> Department of Chemistry, Korea University, Seoul 02841, Republic of Korea

**Corresponding Authors**

\*Hee-Kyung Kim (hkim11@kaeri.re.kr), \*Kyungwon Kwak (kkwak@korea.ac.kr)

## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

Table S1. pKa values of the examined carboxylic ligands

Ligands	I = 0.1 m <sup>a</sup>		I = 1.05 m	
	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a1</sub>	pK <sub>a2</sub>
Mal	2.65	5.27	2.49 <sup>b</sup>	5.00 <sup>b</sup>
Suc	3.99	5.24	3.95 <sup>b</sup>	4.88 <sup>b</sup>
Glu	4.19	5.06		
Adi	4.26	5.04		
Mala			3.15 <sup>c</sup>	4.45 <sup>c</sup>
Ac			4.58 <sup>a</sup>	

<sup>a</sup>Taken from NIST database.<sup>1</sup>

<sup>b</sup>Calculated using SIT from the reported values under I = 0 conditions by Gane, R.; Ingold, C. K.<sup>2</sup>

<sup>c</sup>Reported under = 1.05 m NaCl at 25°C.<sup>3</sup>

Table S2. Binary ion interaction coefficients ( $\epsilon(i,j)$ ) used in this study

Binary ion interaction coefficients		Ref. <sup>4-6</sup>
$\epsilon(\text{H}^+, \text{ClO}_4^-)$	$0.14 \pm 0.02$	4
$\epsilon(\text{Am}^{3+}, \text{ClO}_4^-)$	$0.49 \pm 0.03$	4
$\epsilon(\text{Am}(\text{Ox})^+, \text{ClO}_4^-)$	$0.08 \pm 0.05$	4
$\epsilon(\text{Na}^+, \text{Am}(\text{Ox})_2^-)$	$-0.21 \pm 0.08$	4
$\epsilon(\text{Cm}(\text{Ac})^{2+}, \text{ClO}_4^-)$	$0.42 \pm 0.05$	5
$\epsilon(\text{Na}^+, \text{OH}^-)$	$0.04 \pm 0.01$	4

$\epsilon(\text{Na}^+, \text{HOx}^-)$	$-0.07 \pm 0.01$	4
$\epsilon(\text{Na}^+, \text{Ox}^{2-})$	$-0.08 \pm 0.01$	4
$\epsilon(\text{Na}^+, \text{HSucc}^-)$	0.02	6
$\epsilon(\text{Na}^+, \text{Succ}^{2-})$	0.09	6

Table S3. NLMO bond order for Am-O<sub>lig</sub> and Am-O<sub>aqua</sub>.

Species	Binding mode	Bond order Am-O <sub>lig</sub>	Bond order Am-O <sub>aqua</sub>
Ox 1:1	side-on 5-membered ring	0.0549	0.0154
		0.0509	0.0079
		0.0508	0.0010
Mal 1:1	side-on 6-membered ring	0.0502	0.0163
		0.0548	0.0115
Suc 1:1	end-on 4-membered ring	0.0490	0.0195
Glu 1:1		0.0434	0.0196
Adi 1:1		0.0429	0.0194
Ac 1:1		0.0375	0.0190
[Am(H <sub>2</sub> O) <sub>9</sub> ] <sup>3+</sup>		-	0.0297

The NLMO bond order for Am-O<sub>lig</sub> indicates the calculated bonding order without considering anti-bond. The bond order data of Am-O<sub>aquo</sub> shows the bonding strength between Am and oxygen in water, which confirms that the bonding become weaker (decreased bonding order induced by dicarboxylates) after binding with dicarboxylates. In general, its bonding order (Am-O<sub>aquo</sub>) decreases more for the side-on chelating structures than for the end-on chelating structures, which confirms tighter binding by side-on oriented ligands.

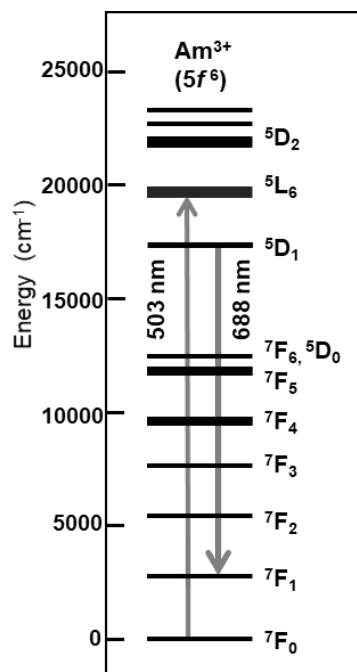


Figure S1. Electronic energy states of  $\text{Am}^{3+}$  ( $5f^6$ ). The arrows indicate major electronic transitions.<sup>7-9</sup> Due to the strong spin-orbit couplings of Am(III), only  $J$  remains as a good quantum number for these energy levels.

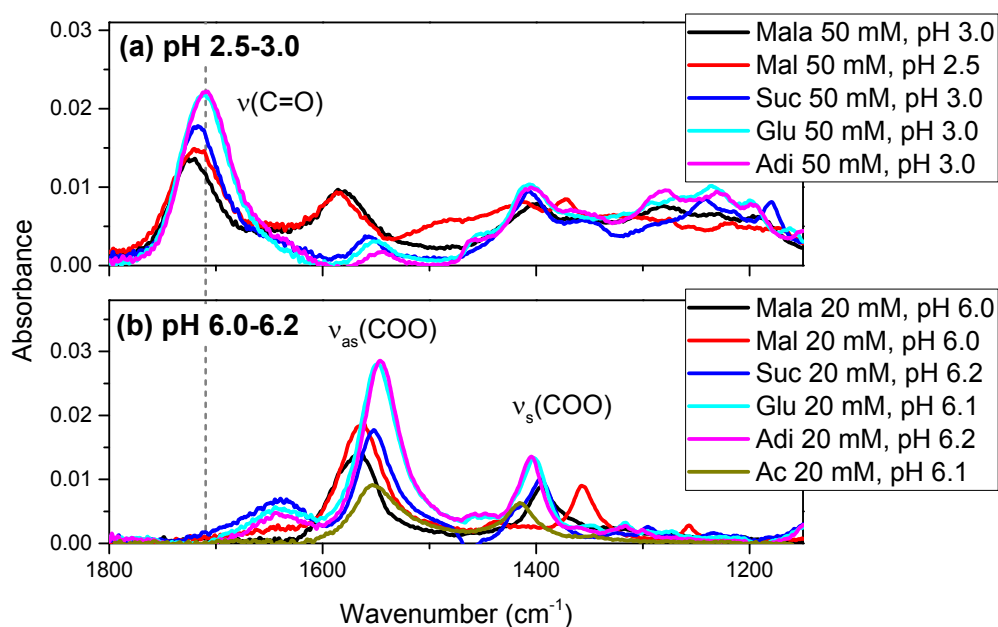


Figure S2. ATR-FTIR spectra of carboxylic ligands under (a) pH 2.5–3.0 and (b) pH 6.0–6.2. At pH above 6, the C=O stretching band ( $1710\text{--}1720\text{ cm}^{-1}$ ) disappeared and strong asymmetric ( $v_{\text{as}}(\text{COO})$   $1540\text{--}1570\text{ cm}^{-1}$ ) and symmetric ( $v_{\text{s}}(\text{COO})$   $1350\text{--}1420\text{ cm}^{-1}$ ) stretching bands appeared. These data indicate that all the carboxyl groups were deprotonated under pH  $\sim 6$  conditions.

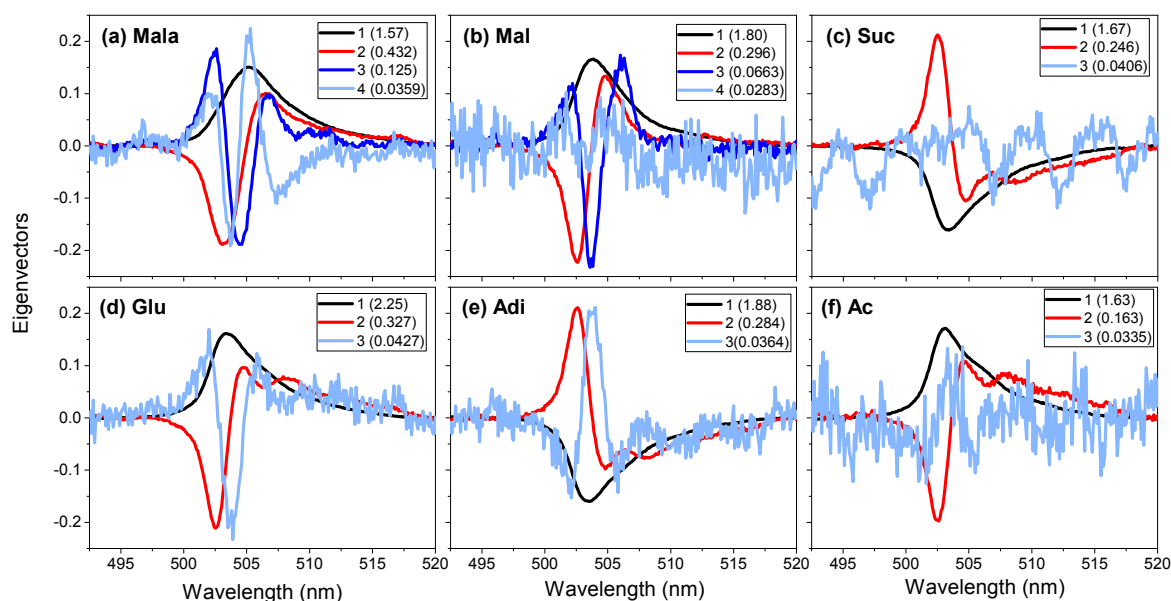


Figure S3. Eigenvector plots obtained from the factor analysis of the absorption spectra using HypSpec program. The relatively noisy eigenvector plots (in blue) are indicative of non-absorbing species. The results of the factor analysis suggest that there are three absorbing species ( $\text{Am}^{3+}$ , 1:1, and 1:2 complexes) for Mal and Mala, and two absorbing species ( $\text{Am}^{3+}$  and 1:1 complexes) for Suc, Glu, Adi, and Ac under our experimental conditions.

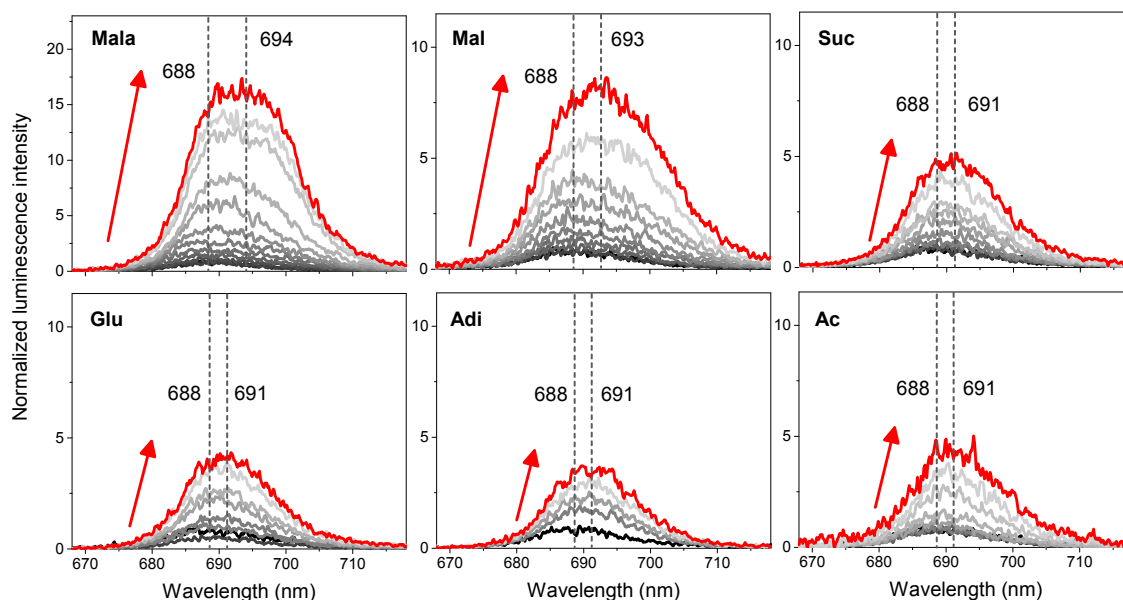


Figure S4. Luminescence spectra measured as a function of ligand concentrations. The samples are the same series as that in Fig. 2. Note that the intensity scale for Mala is twice that of the others. Each spectrum was obtained by accumulating the luminescence signals from 500 laser pulses. The ICCD gate opening was delayed by 15 ns after a laser pulse with a width of 500 ns. The luminescence intensities are normalized to the maximum peak intensity of  $1 \mu\text{M Am}^{3+}$ .

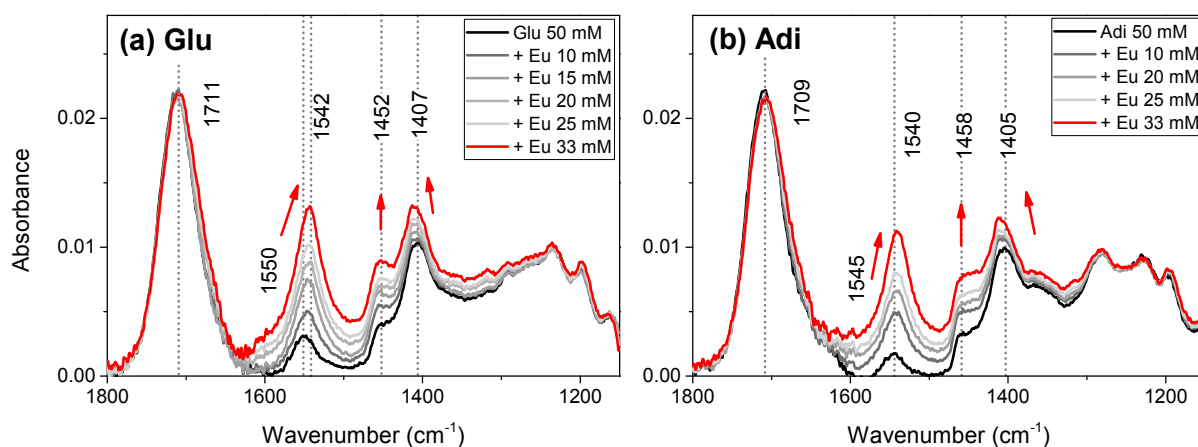


Figure S5. IR spectra of (a) Glu and (b) Adi with increase in Eu concentration under pH 3.

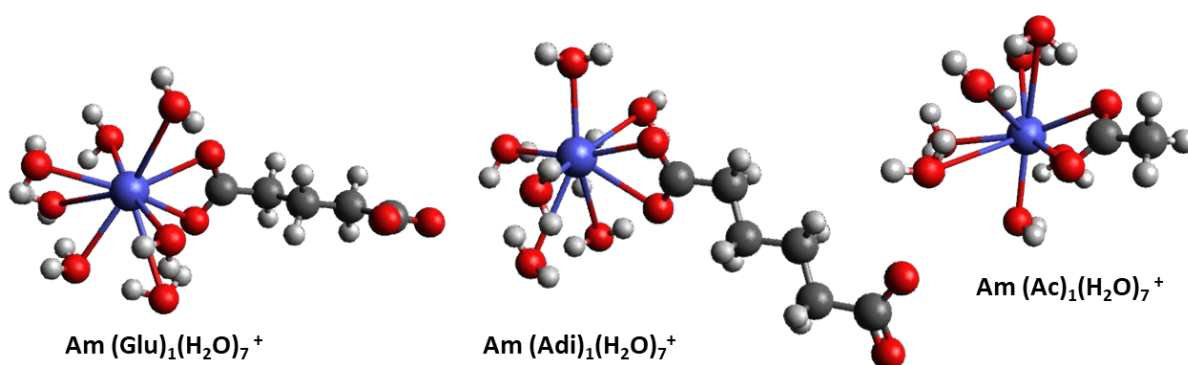


Figure S6. DFT-calculated structures of Am(III)-Glu, Adi, and Ac complexes

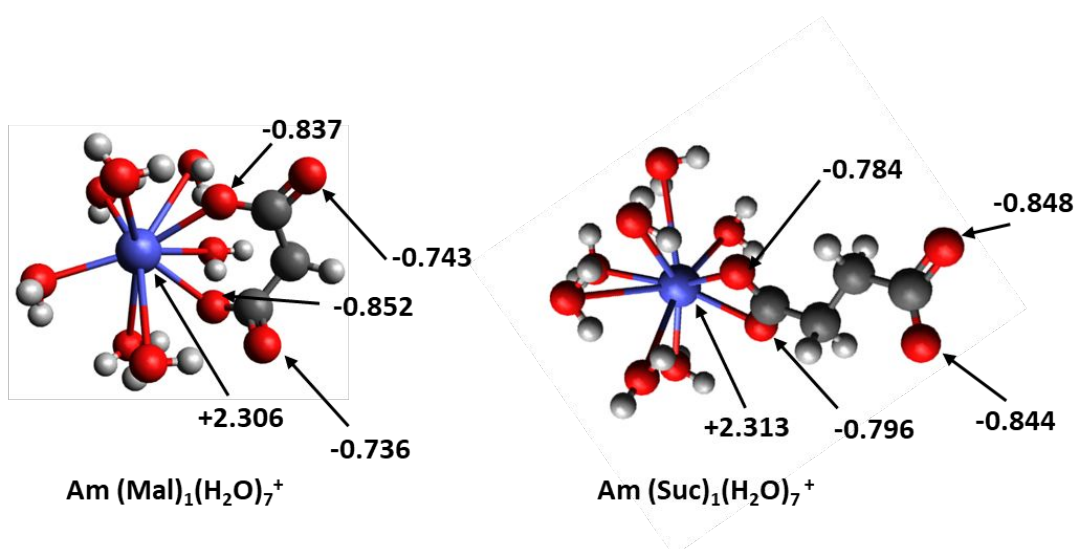


Figure S7. NPA charges of Am(Mal)<sup>+</sup> and Am(Suc)<sup>+</sup> estimated by DFT calculations

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