Electronic Supplementary Information (ESI)

for

Visible-NIR absorption spectroscopy study of the formation of ternary plutonyl(VI) carbonate complexes

Yongheum Jo[a], Hye-Ryun Cho[b] and Jong-Il Yun[*a]

[a]Department of Nuclear and Quantum Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

[b]Nuclear Chemistry Research Team, Korea Atomic Energy Research Institute, 111 Daedeok-daero 989 beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea

*Correspondence and request for materials should be addressed to J.-I. Yun (email: jiyun@kaist.ac.kr).

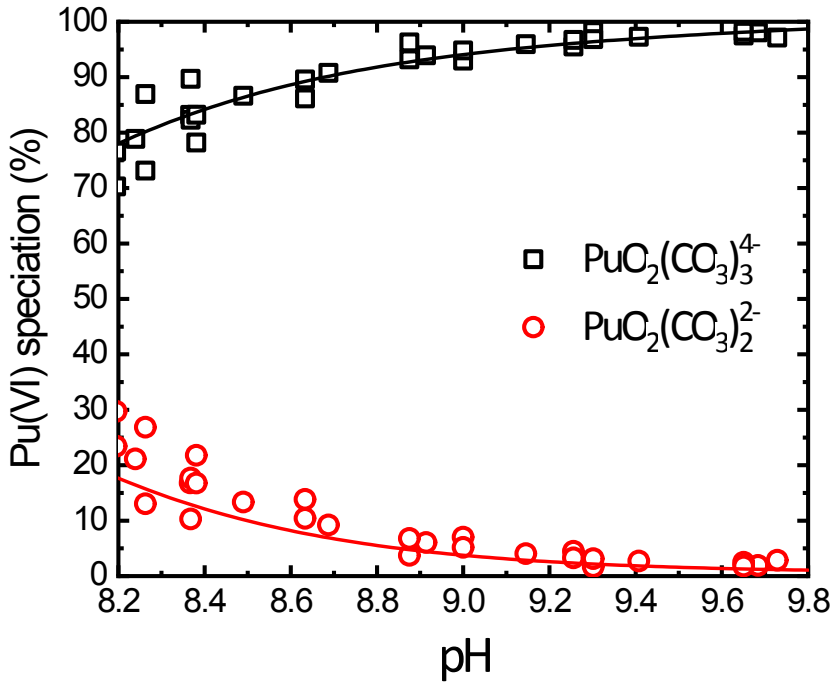

Figure S1. Aqueous Pu(VI) speciation from the Vis-NIR spectrophotometric pH titration at 0.1 M $NaClO_4$. The symbols represent the Pu(VI) speciation determined by the measurements of the spectrophotometric pH titration at each pH point. The lines are calculated using the equilibrium constant of log K = –4.16 for a species transition from $PuO_2(CO_3)_3^{4-}$ to $PuO_2(CO_3)_2^{2-}$ based on the NEA-TDB (Guillaumont, R. et al. Chemical Thermodynamics Vol. 5, Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam, 2003) and the specific ion interaction theory (SIT) with the coefficients reported in the previous work (J.-C. Alexandre, N. Dacheux and J. Aupiais, Radiochimica Acta, 2018, 106, 801).

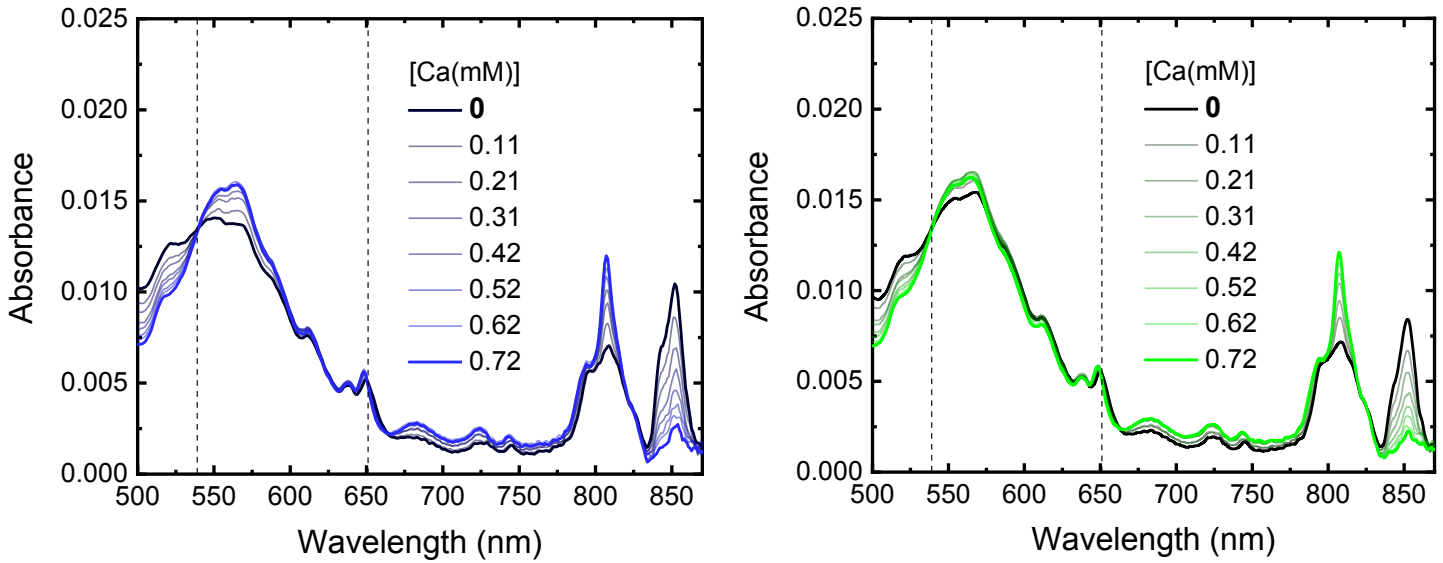

Figure S2. Comparison of results from the spectrophotometric Ca^{2+} titration of plutonium carbonate systems at pH 7.9 (left) and pH 8.2 (right) ([Pu(VI)] = 0.39 mM, $[CO_3^{2-}]_{total}$ = 17 mM, $[Ca^{2+}]$ = 0 to 0.72 mM, and I = 0.1 M $NaClO_4$) with increasing Ca^{2+} ion concentration in the wavelength range of 500 – 870 nm. The isosbestic points at 540 nm 651 nm (dashed line) remain consistent at both pHs, providing that the simultaneous interaction of Ca^{2+} with $PuO_2(CO_3)_3^{4-}$ and $PuO_2(CO_3)_2^{2-}$ are unlikely.

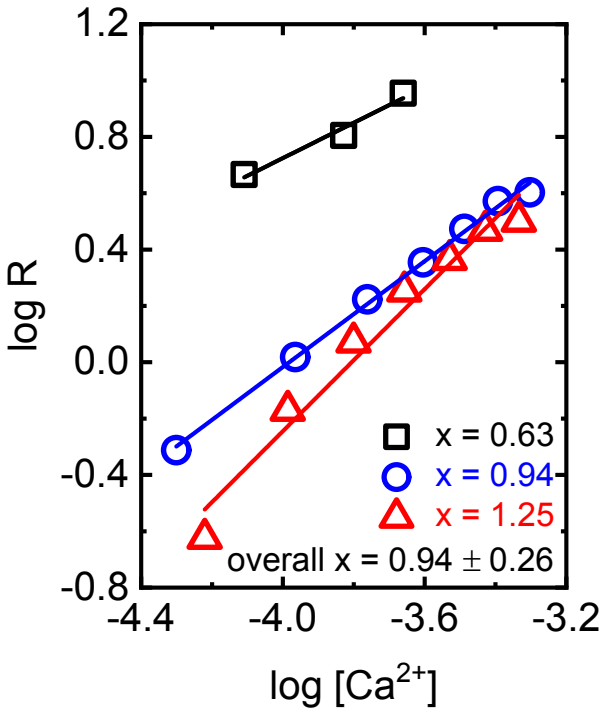

Figure S3. The results of the triplicate slope analysis (log R *vs.* log [Ca^{2+}]) with slopes (x), which represent the stoichiometric number of the complexed Ca^{2+} ions obtained from linear regression. [Ca^{2+}] on the x-axis is determined by the subtraction of the consumed [Ca^{2+}] by the complexation assuming x = 1 from the added $[Ca^{2+}]_{total}$ concentration. The negative value of [Ca^{2+}] by the subtraction at low $[Ca^{2+}]_{total}$ is excluded from the analysis.

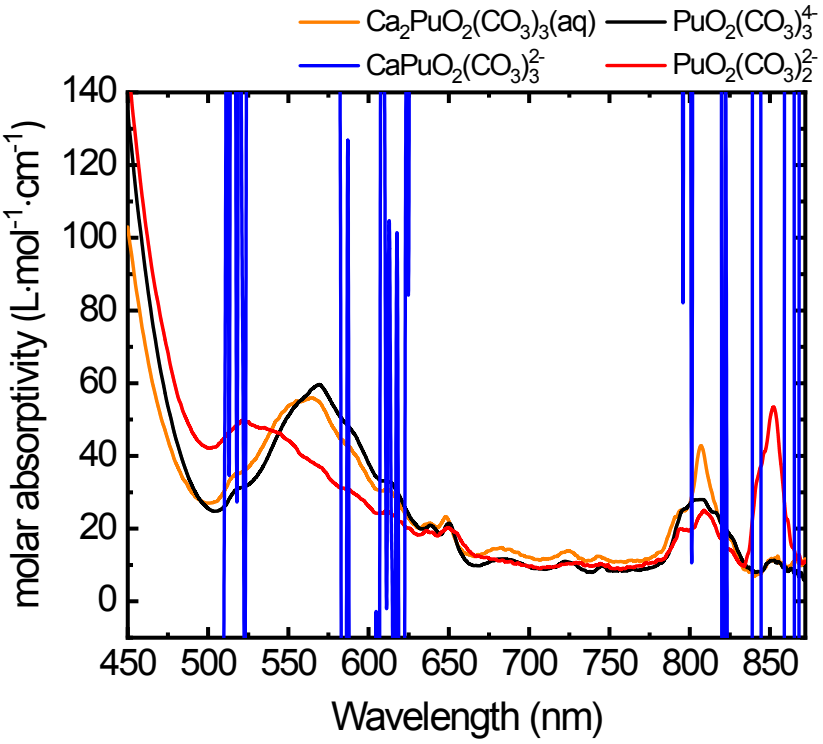

Figure S4. Calculation of absorption spectra of the plutonyl(VI) carbonate species from the results of the spectrophotometric Ca^{2+} titration ([Pu(VI)] = 0.39 mM, $[CO_3^{2-}]_{total}$ = 17 mM, $[Ca^{2+}]$ = 0 to 0.72 mM, pH 7.9, and I = 0.1 M $NaClO_4$) based on a chemical model assuming the formations of $CaPuO_2(CO_3)_3^{2-}$ and $Ca_2PuO_2(CO_3)_3(aq)$. The calculated absorption spectra of $CaPuO_2(CO_3)_3^{2-}$ is largely fluctuating and thus the formation constants from $PuO_2(CO_3)_3^{4-}$ of log K = 8.41 and 1.42 for di-Ca^{2+} and mono-Ca^{2+} species, respectively, are implausible. It indicates failure of the improper chemical model with an inclusion of $Ca_2PuO_2(CO_3)_3(aq)$.

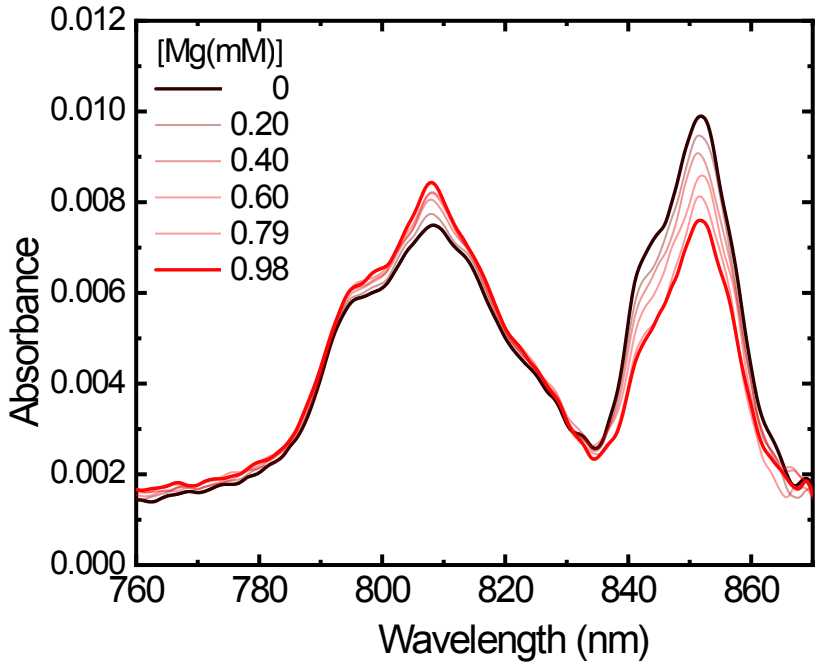

Figure S5. Representative results of spectrophotometric Mg^{2+} titration for plutonyl(VI) carbonate system ([Pu(VI)] = 0.36 mM, $[CO_3^{2-}]_{total}$ = 17 mM, $[Mg^{2+}]$ = 0 to 0.98 mM, pH 7.9, and I = 0.1 M $NaClO_4$) with increasing Mg^{2+} concentration in the wavelength range of 500 – 870 nm.

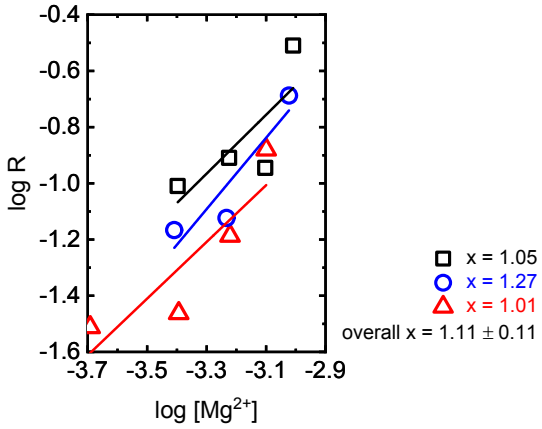

Figure S6. The results of the triplicate slope analysis (log R vs. log [Mg^{2+}]) with the slope (x) representing the stoichiometric number of complexed Mg^{2+} obtained from linear regression. [Mg^{2+}] on the x-axis is determined by the subtraction of consumed [Mg^{2+}] by the complexation assuming x = 1 from added $[Mg^{2+}]_{total}$ concentrations.

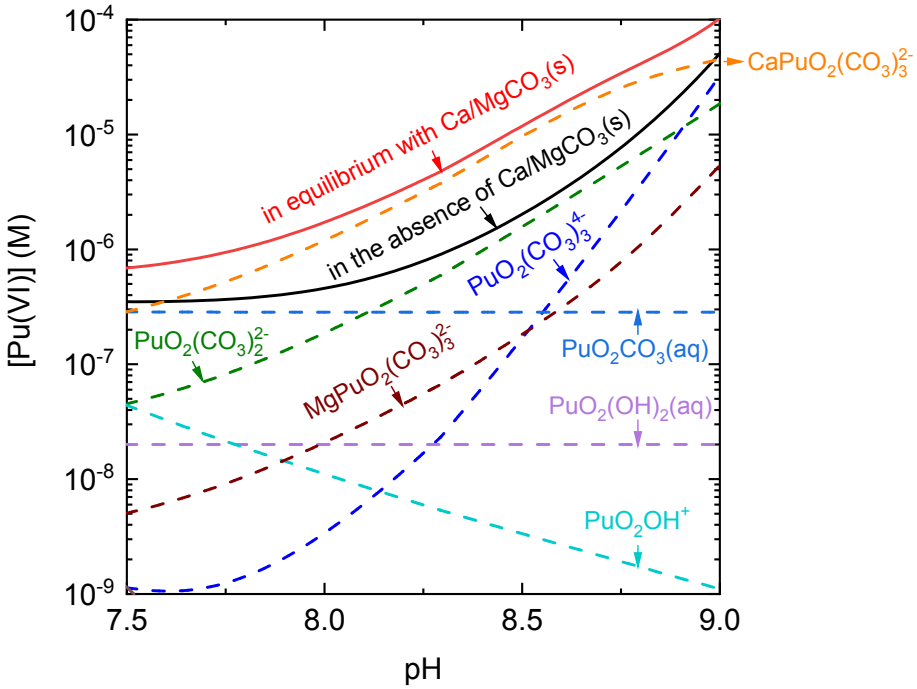

Figure S7. Calculated Pu(VI) solubility (solid line) in aqueous solutions in the presence and absence of Ca/$MgCO_3$(s) (calcite, magnesite, and dolomite). Dashed lines represent the concentrations of Pu(VI) species in equilibrium with Ca/$MgCO_3$(s). The calculation was performed by the identical method used for Figure 3. For the details of calculation, see the Section 2.4 in the main text.