ウラン(VI)選択性沈殿剤としての架橋ピロリドン誘導体の開発

○風間 裕行, 池田 泰久, 鷹尾 康一朗
東工大・先導原研

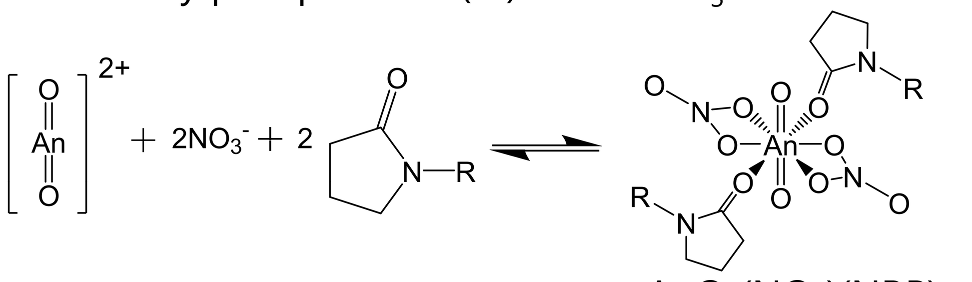
Introduction

- **Current Nuclear Energy System**
  - Exclusively Uranium Fuel
  - Scarcity of U Resources
- **Thorium Fuel Cycle**
  - Th is 3-4 times more abundant than U.
  - ^{232}Th (fertile) + n → ^{233}Th → ^{233}Pa → ^{233}U (fissile)
  - $^{233}U/^{232}Th$ Separation→ Solvent Extraction (1950's ～)
  - Not Very Efficient unlike U/Pu Separation

Necessary to Innovate Concept and Methodology of U/Th Separation in Spent Th-Fuel Reprocessing

Previous Study

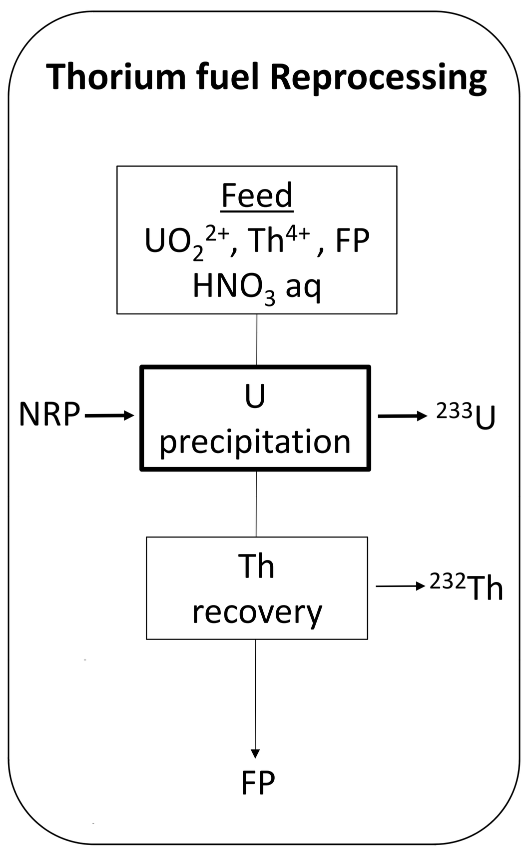
N-alkylated 2-pyrrolidone derivatives (NRPs) can selectively precipitate An(VI) from HNO_3 solutions



Reprocessing System Based on Precipitation Method
- Smaller Amount of Additives
- Simple Process

Most Stable Oxidation State in HNO_3(aq) : **U(VI), Th(IV)**

Applicable to $^{233}U/^{232}Th$ Separation in Spent Th Fuel Reprocessing

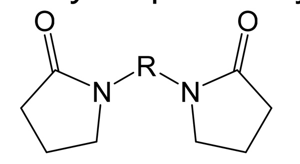


Molecular Design of NRPs

	Demand	Requirement	Solution
1	U/Th Selectivity	No Th^{4+} Precipitation	Low Hydrophobicity
2	Efficient Recovery of U	Low UO_2^{2+} Solubility	High Hydrophobicity

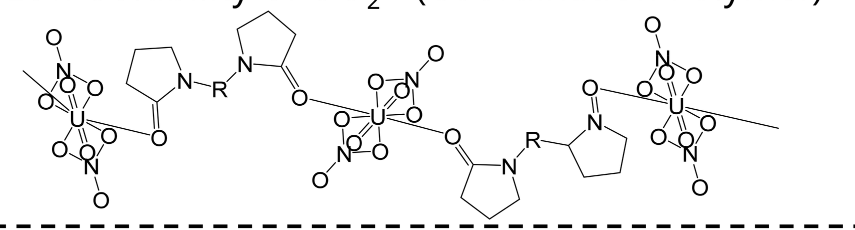
Double-Headed NRP

1. Low Hydrophobicity (Two Amide Groups)



Double-Headed NRP

2. Low Solubility of UO_2^{2+}(Coordination Polymer)

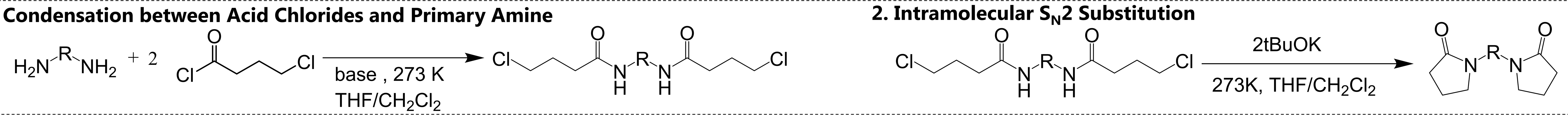


Objective

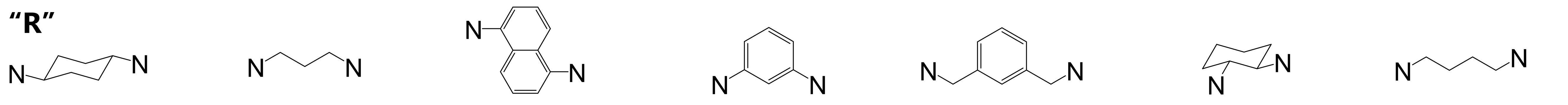
- **Synthesis and Characterization of Uranyl Nitrate Complexes with Various Double-Headed NRPs**
- **Evaluation of Capability of NRPs as Precipitant for UO_2^{2+} from Viewpoint of Structural Chemistry**

Synthesis of NRPs

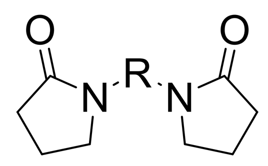
1. Condensation between Acid Chlorides and Primary Amine **2. Intramolecular S_N2 Substitution**



- **Selected Bridging Moieties "R"**



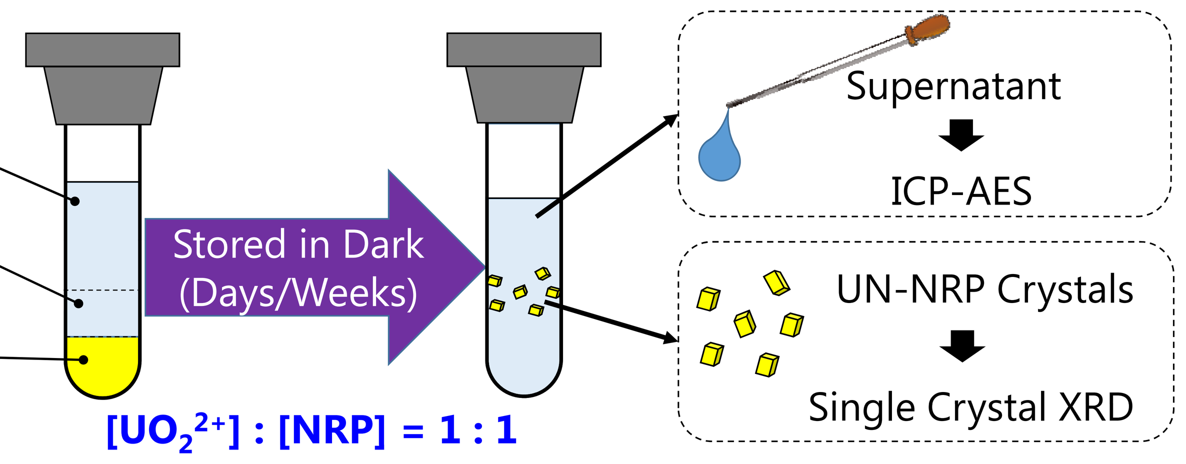
R=



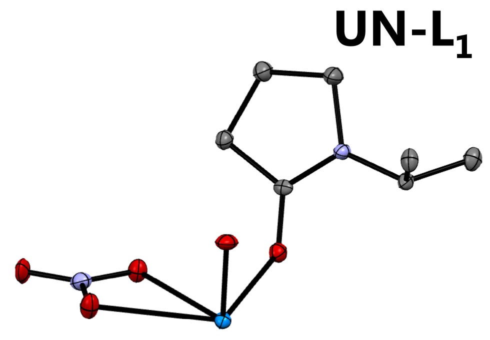
	L_1	L_2	L_3	L_4	L_5	L_6	L_7
	Colorless Solid	Yellow Oil	Colorless Solid	Colorless Solid	Yellow Oil	Colorless Solid	Colorless Solid
	(yield:81%)	(yield:61%)	(yield:79%)	(yield:77%)	(yield:42%)	(yield:44%)	(yield:43%)
	log P = -0.18	log P = -0.85	log P = n.a.	log P = 0.46	log P = 0.33	log P = 0.39	log P = -0.58
	DN = 28.0	DN = 27.2	DN = 26.7	DN = 23.8	DN=27.3	DN = 24.3	DN = 28.0

- **Donor Number (DN)** : a scale of Lewis basicity
- **log *P*** : logarithmic value of partitioning coefficient between water and 1-octanol

Synthesis & Characterization of $UO_2(NO_3)_2NRP$ (UN-NRP)

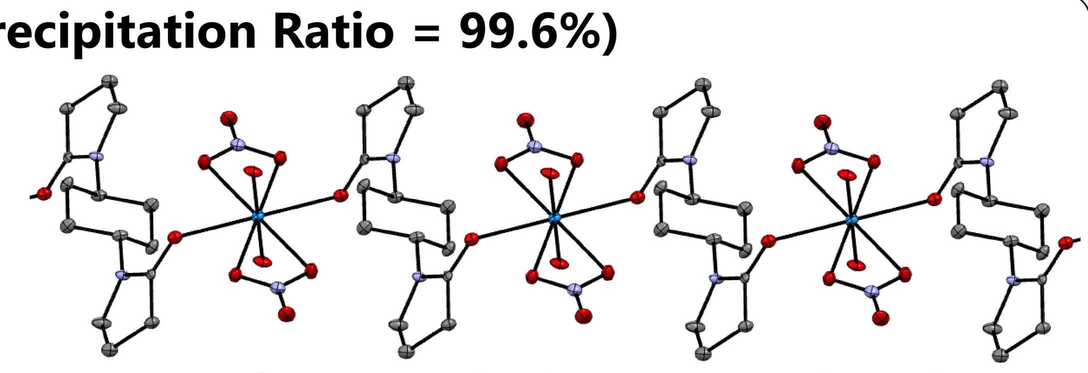


UN-L_1 (Precipitation Ratio = 99.6%)



Asymmetric Unit

●:C, ●:N, ●:O, ●:U



Only One U site in Asymmetric Unit

Crystallographic Data of $UO_2(NO_3)_2(L_1)$:
$C_{14}H_{22}N_4O_{10}U$; triclinic, *P*-1(#2);
a = 5.8965(4), b = 7.6330(5), c = 11.0287(8) Å,
α = 76.843(5), β = 84.476(6), γ= 76.228(5)°;
V = 468.98(6) Å^3; Z = 1; D_{calcd} = 2.281 g/cm^3;
m = 9.306 mm^{-1}; T = 93 K;
R = 0.0353 (F^2 > 2s); wR = 0.0873 (all);

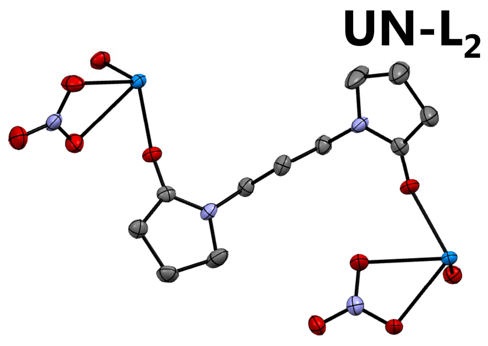
Elemental Analysis

	C	H	N
calcd. / %	26.10	3.44	8.69
found/ %	26.30	3.34	8.65

Raman & IR (cm^{-1})

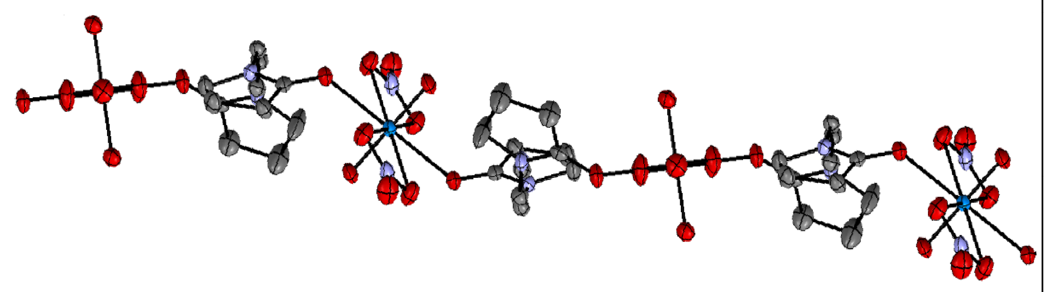
$\nu_{symmetric}$	$\nu_{asymmetric}$
852	927

UN-L_2 (Precipitation Ratio = 63.8%)



Asymmetric Unit

●:C, ●:N, ●:O, ●:U



Two Different U sites in Asymmetric Unit

Crystallographic Data of $UO_2(NO_3)_2(L_2)$:
$C_{11}H_{18}N_4O_{10}U$; triclinic, *P*-1(#2);
a = 5.998(1), b = 11.534(2), c = 13.224(2) Å,
α = 100.169(7), β = 95.142(7), γ = 100.614(7)°;
V = 878.0(3) Å^3; Z = 2; D_{calcd} = 2.286 g/cm^3;
m = 9.306 mm^{-1}; T = 183 K;
R = 0.0298 (F^2 > 2s); wR = 0.0817 (all);

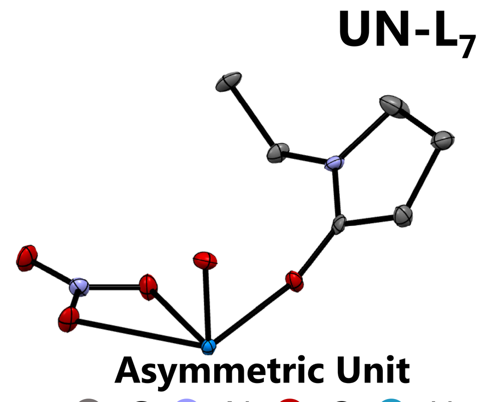
Elemental Analysis

	C	H	N
calcd. / %	21.86	2.94	9.27
found/ %	21.71	3.11	8.87

Raman & IR (cm^{-1})

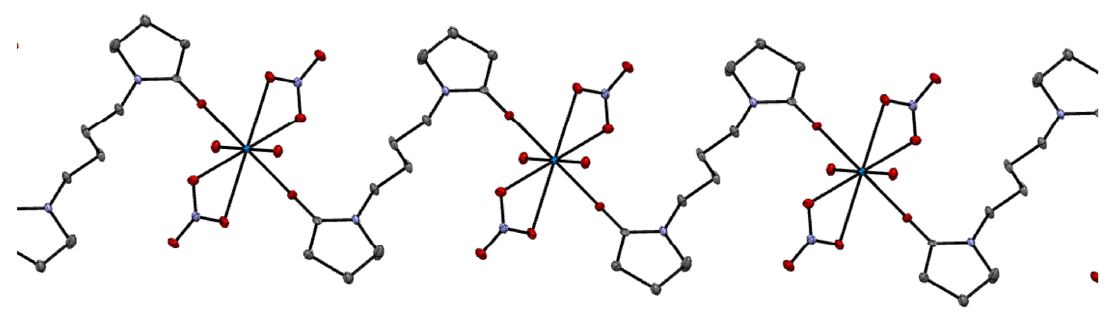
$\nu_{symmetric}$	$\nu_{asymmetric}$
852	930

UN-L_7 (Precipitation Ratio = 94.1%)



Asymmetric Unit

●:C, ●:N, ●:O, ●:U



Only One U site in Asymmetric Unit

Crystallographic Data of $UO_2(NO_3)_2(L_7)$:
$C_{12}H_{20}N_4O_{10}U$; triclinic, *P*-1(#2);
a = 5.8789(6), b = 7.7353(9), c = 10.3183(9) Å,
α = 76.285(5), β = 76.522(5), γ = 78.018(6)°;
V = 437.49(8) Å^3; Z = 1; D_{calcd} = 2.347 g/cm^3;
m = 9.306 mm^{-1}; T = 93 K;
R = 0.0284 (F^2 > 2s); wR = 0.0676 (all);

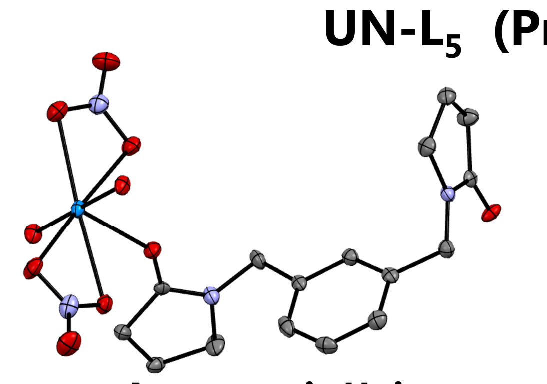
Elemental Analysis

	C	H	N
calcd. / %	23.31	3.26	9.06
found/ %	23.26	3.18	8.87

Raman & IR (cm^{-1})

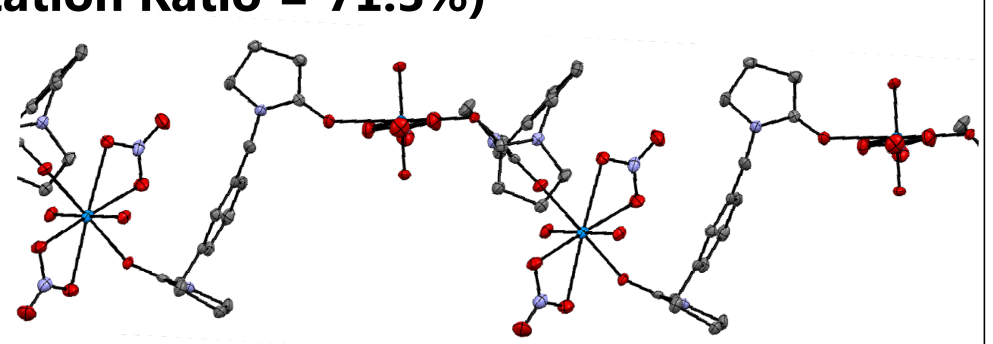
$\nu_{symmetric}$	$\nu_{asymmetric}$
852	928

UN-L_5 (Precipitation Ratio = 71.3%)



Asymmetric Unit

●:C, ●:N, ●:O, ●:U



- Only One U site in Asymmetric Unit
- 2_1 screw axis is present.

Crystallographic Data of $UO_2(NO_3)_2(L_5)$:
$C_{16}H_{20}N_4O_{10}U$; monoclinic, $P2_1/n$(#14);
a = 11.5236(4), b = 9.4793(4), c = 19.7364(7) Å,
β = 102.542(7)°;
V = 2104.47(14) Å^3; Z = 4; D_{calcd} = 2.103 g/cm^3;
m = 9.306 mm^{-1}; T = 93 K;
R = 0.0543 (F^2 > 2s); wR = 0.1149 (all);

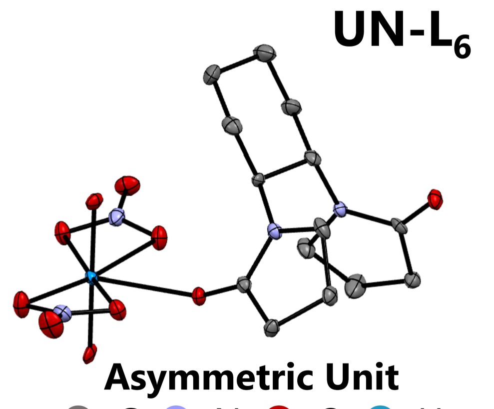
Elemental Analysis

	C	H	N
calcd. / %	28.84	3.03	8.41
found/ %	28.79	2.97	7.96

Raman & IR (cm^{-1})

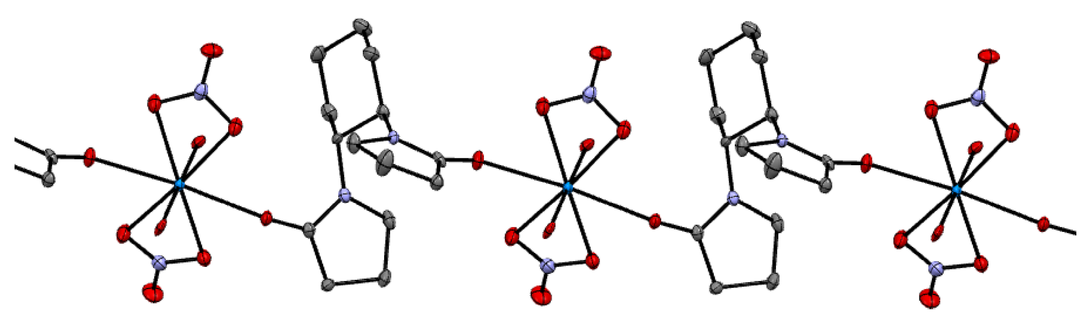
$\nu_{symmetric}$	$\nu_{asymmetric}$
854	935

UN-L_6 (Precipitation Ratio = 91.8%)



Asymmetric Unit

●:C, ●:N, ●:O, ●:U



Only One U site in Asymmetric Unit

Crystallographic Data of $UO_2(NO_3)_2(L_6)$:
$C_{14}H_{22}N_4O_{10}U$; triclinic, *P*-1(#2);
a = 9.9552(6), b = 10.0698(4), c = 10.1724(5) Å,
α = 90.872(6), β = 106.642(8), γ = 90.426(6) °;
V = 976.85(9) Å^3; Z = 2; D_{calcd} = 2.191 g/cm^3;
m = 9.306 mm^{-1}; T = 93 K;
R = 0.0345 (F^2 > 2s); wR = 0.0796 (all);

Elemental Analysis

	C	H	N
calcd. / %	26.10	3.44	8.69
found/ %	26.03	3.31	8.45

Raman & IR (cm^{-1})

$\nu_{symmetric}$	$\nu_{asymmetric}$
854	931

Important Precipitation Factor
- ➢ **High Symmetry of UN-NRPs**
- ➢ **Moderate Flexibility of Bridging Moiety**

Conclusion

- UN-L_1, UN-L_2, UN-L_5, UN-L_6 and UN-L_7 were synthesized and characterized by single crystal X-Ray Diffraction, elemental analysis, IR and Raman spectra.
- High symmetry of UN-NRPs and moderate flexibility of bridging moiety are important for efficient precipitation of U(VI) in HNO_3 solution.

Future Work

- Precipitation Experiment for Tetravalent Actinides, U(IV) and Th(IV)
- Decontamination Experiments for Simulated FPs, F^- and Al^{3+}

*This study is the result of "Fundamental Study on Simple Reprocessing Method for Spent Thorium Fuels by Using Uranium-Selective Precipitant" entrusted to Tokyo Institute of Technology by MEXT