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Structural Features of Zirconium-Based Metal–Organic Frameworks (MOFs) Affecting Radiolytic Stability

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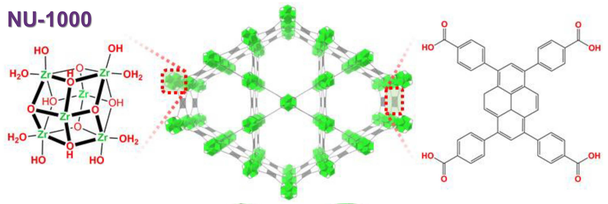
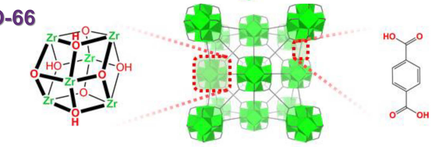
MOFs for Nuclear Waste Cleanup

- To be viable capturing agents under radioactive conditions, MOFs must remain stable under **ionizing radiation**

NU-1000



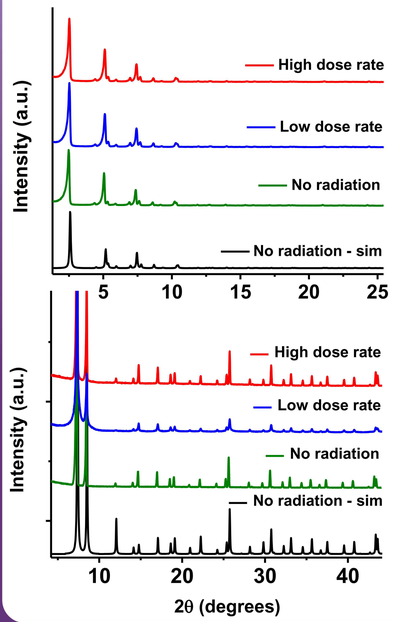
UiO-66



- NU-1000 & UiO-66: MOFs with the same metal absorption cross section but different structural features
- **MOF stability vs. irradiation dose rate**

Varying Crystallinity of NU-1000 and UiO-66 under ^{60}Co-γ Irradiation

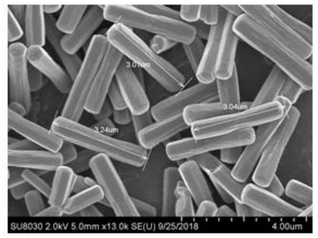
Dose Type	Dose Rate (Gy/min)	Time (min)	Total Dose (Gy)
High/Acute	423.3	23.62	9996.9
Low/Chronic	0.78	4320	3369.6



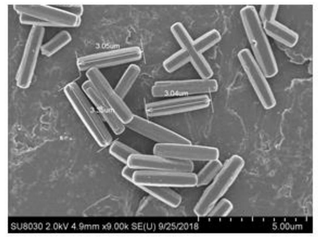
- **NU-1000:** PXRD demonstrates **no apparent response** to gamma irradiation dose rates and retains peak intensity without broadening or loss of peaks

- **UiO-66:** PXRD shows that exposure to the **chronic, low** dose rate appears to **adversely affect** UiO-66

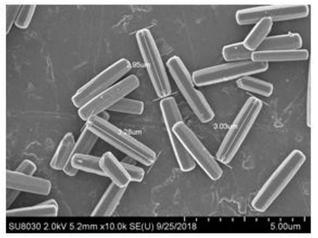
NU-1000 Exhibits Insignificant Radiation Damage While UiO-66 Shows Structural Damage Under Low, Chronic Irradiation Dose Rates



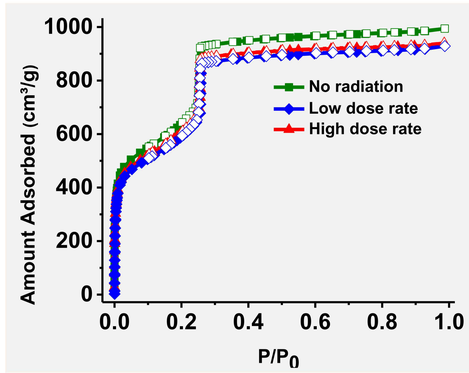
NU-1000, NO radiation



NU-1000, LOW dose rate



NU-1000, HIGH dose rate

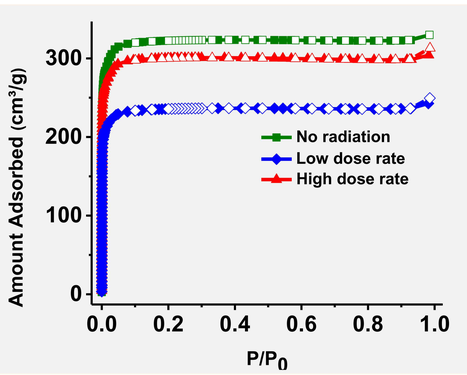


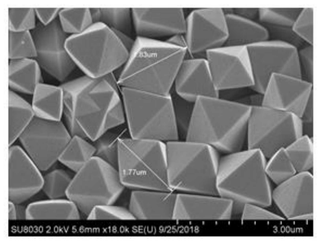
NU-1000

- SEM studies show NU-1000 has **uniformity** in crystal size and generally **unchanged morphology**
- **Slight surface area decrease** from 2160 m^2g^{-1} by **7%** (2005 m^2g^{-1}) and **5%** (2050 m^2g^{-1}) after low and high dose rates, respectively

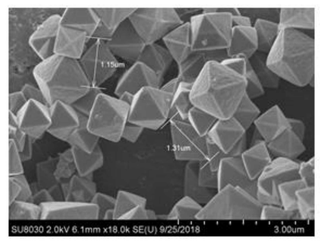
UiO-66

- SEM studies demonstrate a **roughening of UiO-66 crystallite exterior after the low dose rate**
- **Considerable surface area decrease** from 1302 m^2g^{-1} by **27%** (960 m^2g^{-1}) and **7%** (1230 m^2g^{-1}) after low and high dose rates, respectively

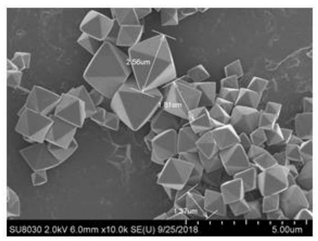




UiO-66, NO radiation



UiO-66, LOW dose rate



UiO-66, HIGH dose rate

MOF Stability and Damage Related to Structural Features

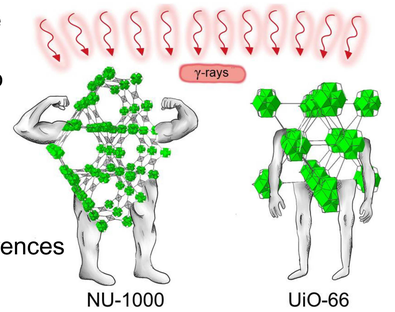
Structural Features	NU-1000	UiO-66	Contribute to Stability
Linker aromaticity	High	Low	---
Linker connectivity	*4	2	High
Node density	*0.15 gcm^{-3}	0.60 gcm^{-3}	Low
Node Connectivity	*8	12	Low
Inter-ligand separation	3.79 Å	4.21 Å	---

- NU-1000 **higher linker connectivity** = more **stable towards cleavage** of the carboxylate oxygen-zirconium bonds
- **Lower density of Zr_6O_8 nodes** in NU-1000 = **absorbs less radiation**
- NU-1000 **low node connectivity** = radiation absorbed by the node **propagates to the dangling -OH and H_2O groups** rather than solely to the linkers

* indicates specific structural features which promote the stability of NU-1000

Conclusions

- NU-1000: **insignificant radiation damage**
- UiO-66: **structural damage** under **low, chronic** dose rates
- Linker connectivity, node density, and node connectivity contribute to **NU-1000 structural stability** under radiation
- **Small scale** structural variations result in **bulk radiation stability** differences between similar MOFs



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