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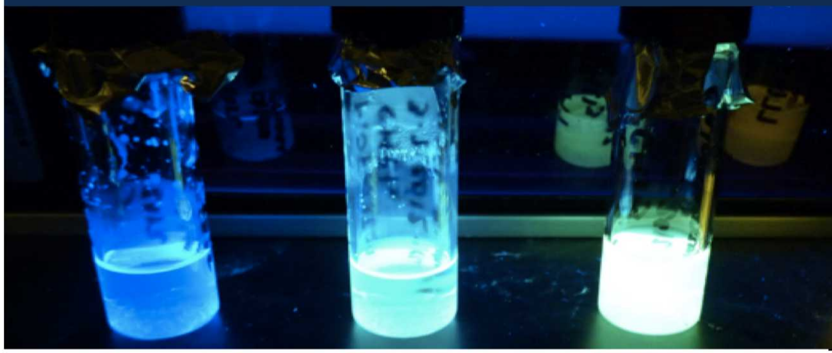

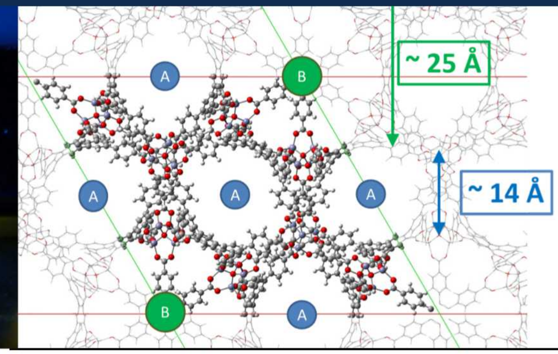

Exploiting MOF Luminosity and Porosity for In-Situ Detection of Xenon Isotopes

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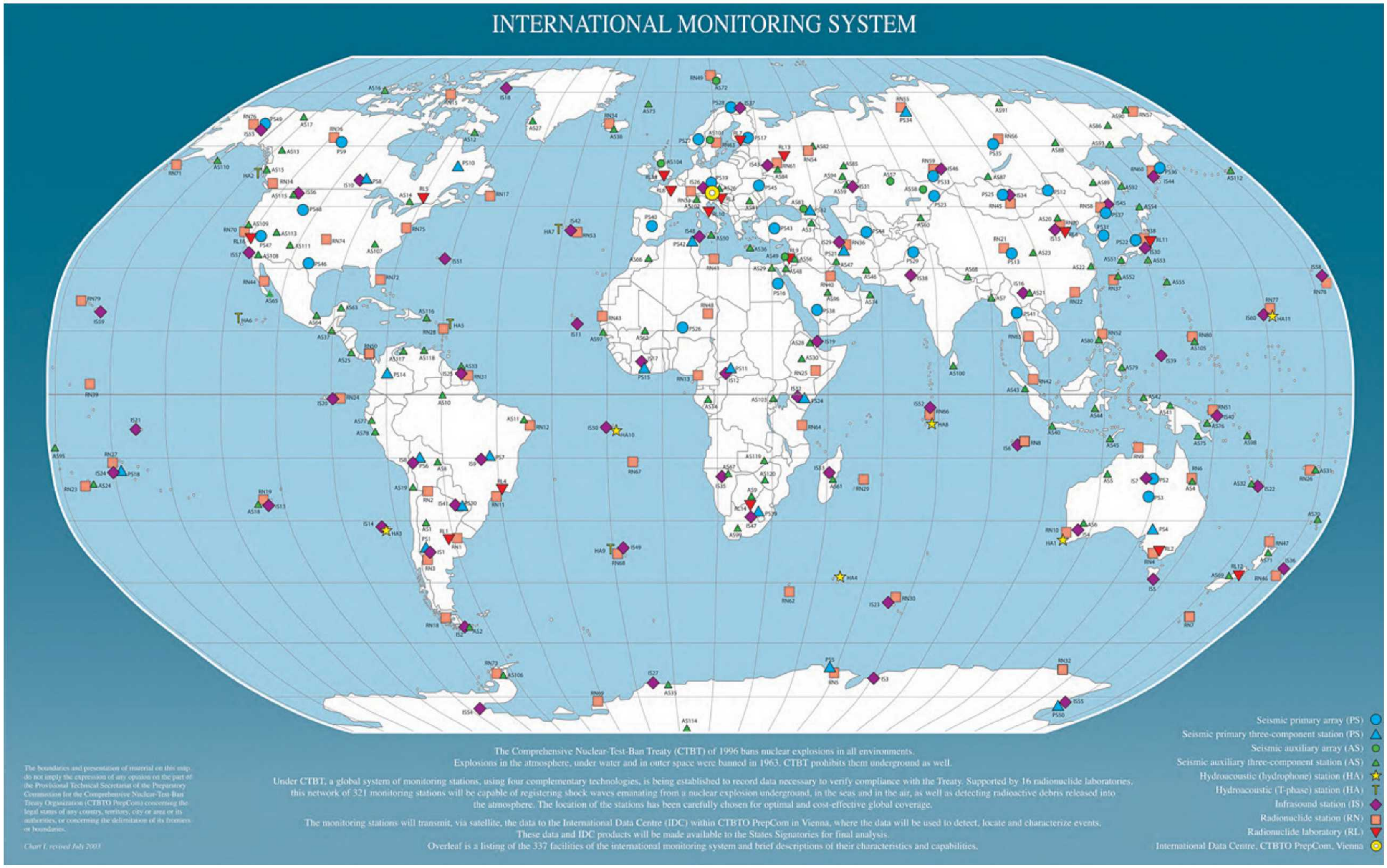
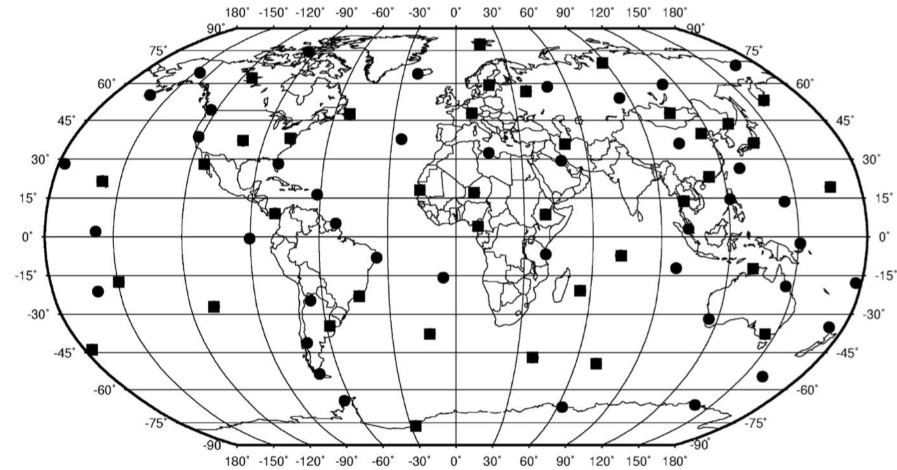
The International Monitoring System (IMS)

321 stations for seismic, airborne radionuclide, hydroaccoustic, and infrasound detection



Airborne radionuclide detection by the IMS



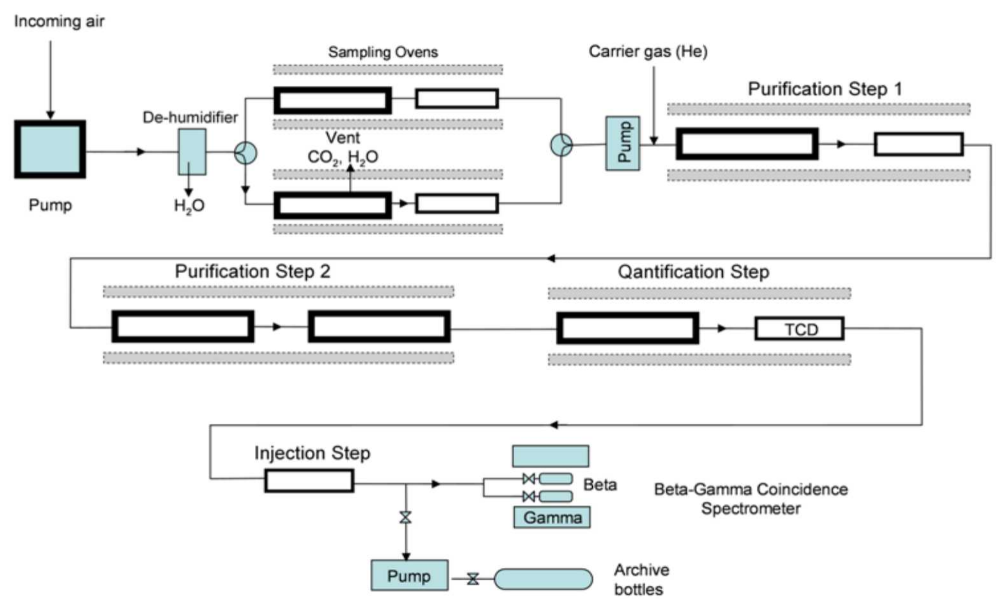
Source terms and events:

- Nuclear reactors
- Fukushima accident
- Medical isotope production facilities
- Nuclear testing in North Korea

Detection of noble gas radioisotopes by IMS monitoring systems

- **^{131m}Xe, ^{133}Xe, ^{133m}Xe, ^{135}Xe**
- Completely automatic commercial systems
- 12-hr collection, followed by 24-hr count

→ Dynamic "real-time" detection, crucial for identifying detonation location by meteorlogical monitoring, is impossible



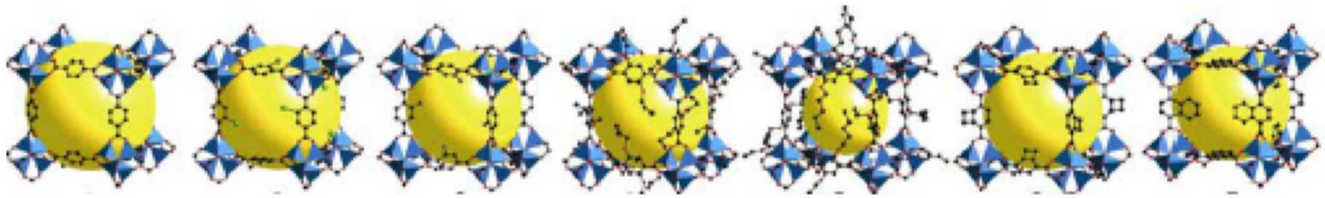
Courtesy, Dr. Ted Boyer, Pacific Northwest National Lab.

Xenon isotopes used for nuclear detonation detection

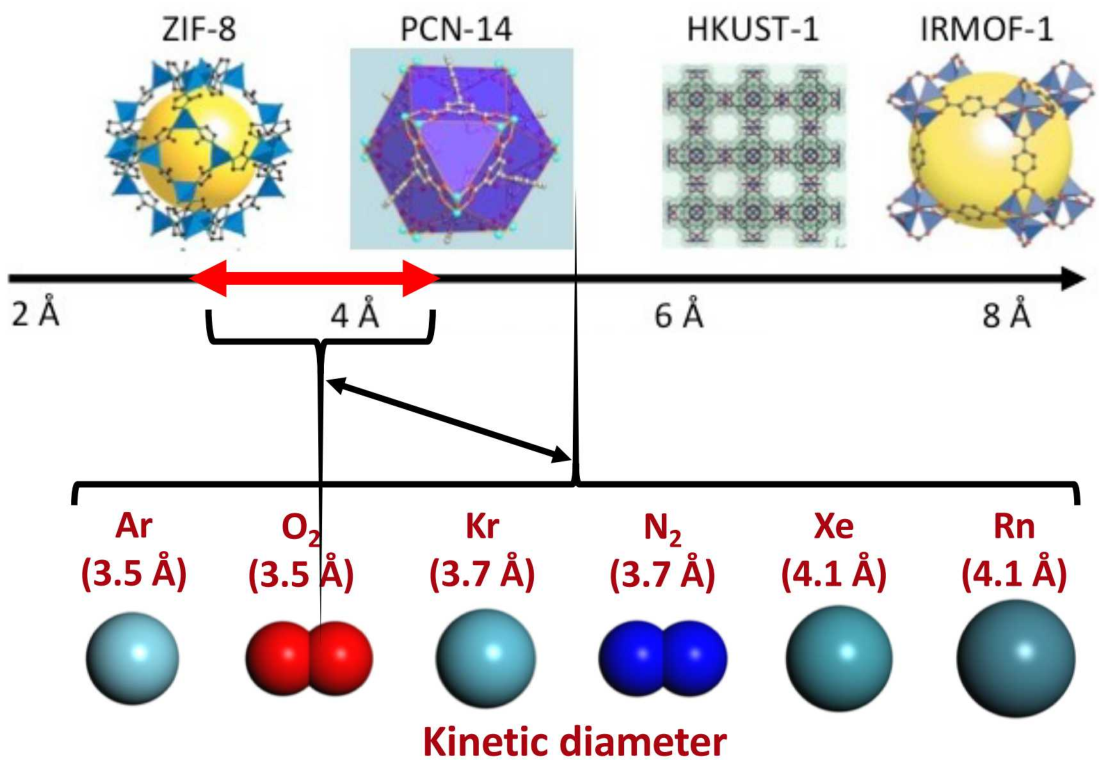
Nuclide	^{131m}Xe	^{133m}Xe	^{133}Xe	^{135}Xe
Fission Yield per kT Pu (Bq)	5×10^{9}	2×10^{13}	2×10^{14}	2×10^{16}
Half-life (days)	11.93	2.19	5.25	0.38
γ Ray (keV)	163.9	233.2	81	249.8
X-rays (keV)	29.5–34.6	29.5–34.6	30.6–36.0	30.6–36.0
β Endpoint (keV)	-	-	346	905
Conversion electron (keV)	129	199	45	214

Multiple isotopes are used to distinguish a detonation from isotopes produced by medical isotope production facility

MOFs are well-known adsorbents for noble gases

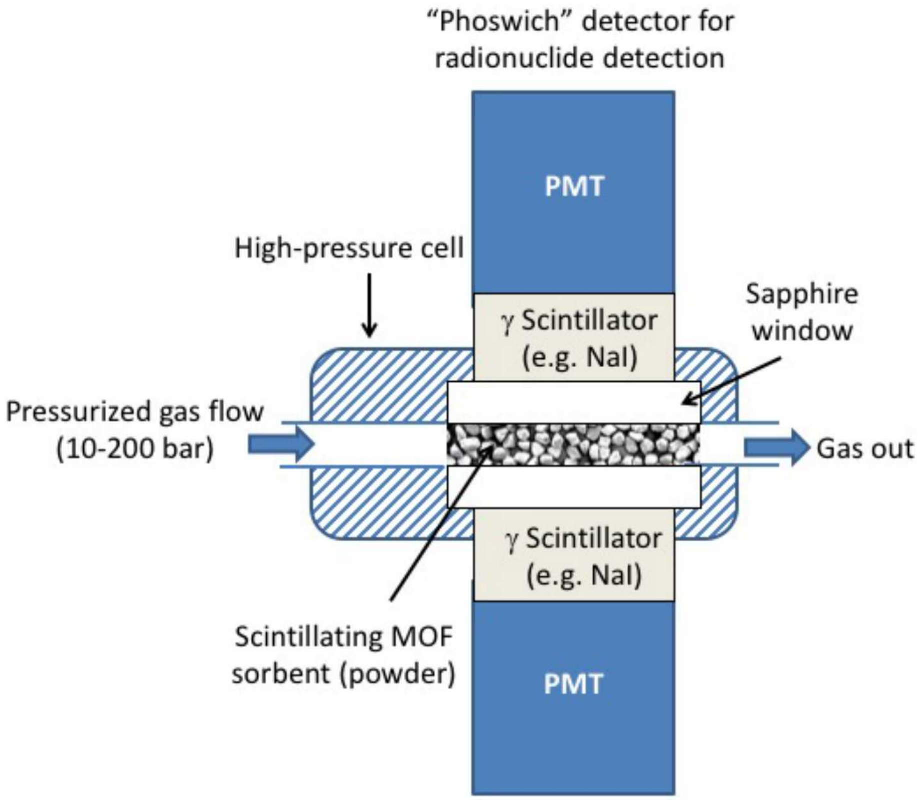


- **Ultrahigh surface areas enable preconcentration of noble gases**
- **Selective gas uptake due to tailorable pore size/chemical environment; e.g.**
  - **(Kr, Xe, or Rn):N_2 > 6**
- **Stable in air to ≥ 200 °C; allows fast sorbent regeneration**



Multi-axis concept for detecting unstable noble gas isotopes

- **Use scintillating MOFs (S-MOFs) as sorbent+detection material**
  1. β-counts above background
  2. Coincident γ energy
  3. Timing distributions
  4. Continuous integrated signal (real time)
- **High-pressure cell (10-100 bar) to increase gas concentration**
- **"Dual Phoswich" detector design**
  - S-MOF sorbent for β particles
  - NaI scintillator for coincident γ particles
  - Discriminates against background muons and γ particles



Detection enhancement factors (GCMC calculations) for MOFs screening CoRE Database
- **Max. absolute Xe uptake (v/v): ~30 – 200 cm^3@STP/cm^3**
- **Excess capacity (v/v): 100 – 180 cm^3@STP/cm^3**
- **Xe/N_2 selectivity: 5 – 28X**
- **Detector geometry 4π β interaction: ~2X**

→ ~400X signal enhancement over conventional continuous air monitor should be feasible

Coincidence detection discriminates background events

APD linear channels

NaI/PMT

APD timing out

APD channels

NaI/PMT channels

APD channels

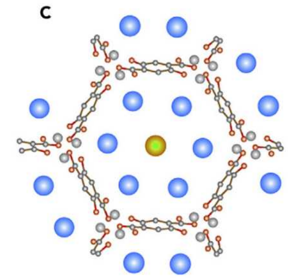
NaI/PMT channels

APD channels

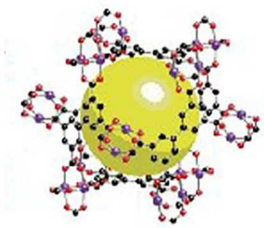
NaI/PMT channels

Although many MOFs have high uptake and selectivity for Xe, most are not luminescent

MOF	Xe Uptake (mmol g^{-1}[a] or mmol Kg^{-1}[b])	Xe Q_{st} (kJ mol^{-1})	Xe/Kr Selectivity
CaSDB (SBMOF-1)	1.4[a] (13.2)[b]	35	16[a]
SBMOF-2	2.06[a]	26.4	10[c]
Ni-MOF-74	4.19[a] (4.8)[b]	22	7.3[c]
$Co_3(HCOO)_6$	2[a]	28	12[d]
HKUST-1	3.3[a]	26.9	8.4[e] (3)[b]
MOF-5	1.98[a]	15	–
FMOF-Cu	0.8[a]	15	2[f]
MFU-4l	1.8[a]	20	4.7[e]
MOF-505	2.2[a]	–	8[g]
SIFSIX-3-Ni	2.51[a]	18.9	–
SIFSIX-3-Fe	2.45[a]	27.4	–
CROFOUR-1-Ni	1.8[a]	37.4	22[c]
CROFOUR-2-Ni	1.6[a]	30.5	15.5[c]
UIO-66	1.58[a]	–	3.8[g]
PCN-14	7.1[a]	17.9	6.5[d]
NOTT-100	6.1[a]	18.6	6.7[d]
NOTT-103	4.1[a]	19.7	5.5[d]
ZIF-8	–	–	1.9
$[Zn(tmz)_2]$	3[a]	23	15.5[f]
MOF-74 Mg	5.58[a]	–	5.92
MOF-74-Co	6.1[a]	–	10.37
MOF-74-Zn	3.88[a]	–	5.76
Porous Organic Cages, Carbons, and Covalent-Organic-Framework-like Materials			
Noria	1.55[a]	24.5–26.9	9.4[a,b]
CC3	2.2[a] (11)[b]	31.3	20.4[a] (16)[b]
COP-4	1.7[a]	–	1.5
Activated Carbon	4.2[a]	–	8
Carbon-Zx	4.42[a]	–	–
Carbon-Z	3.17[a]	–	–



MOF-74



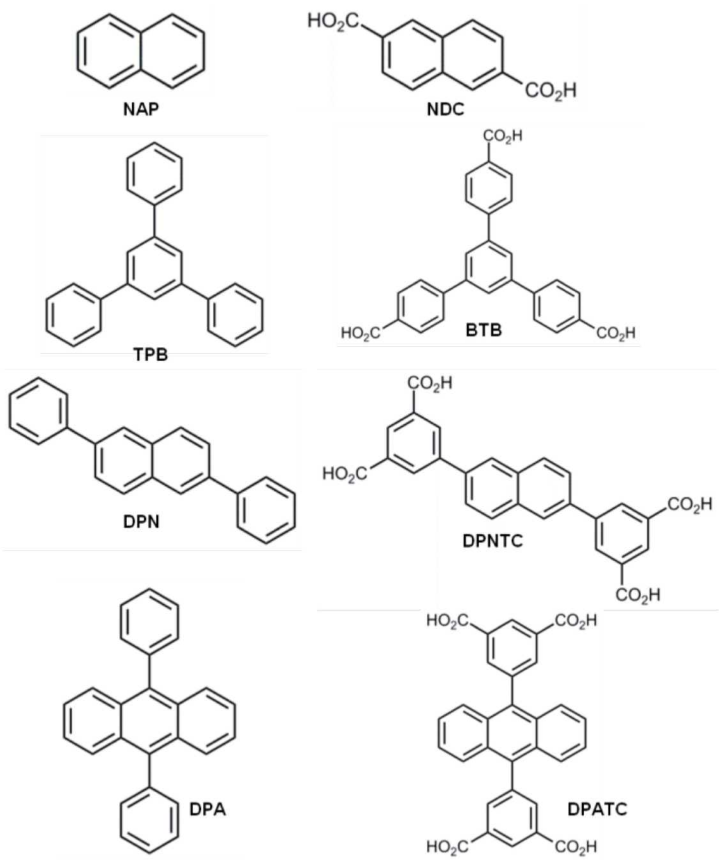
MOF-505

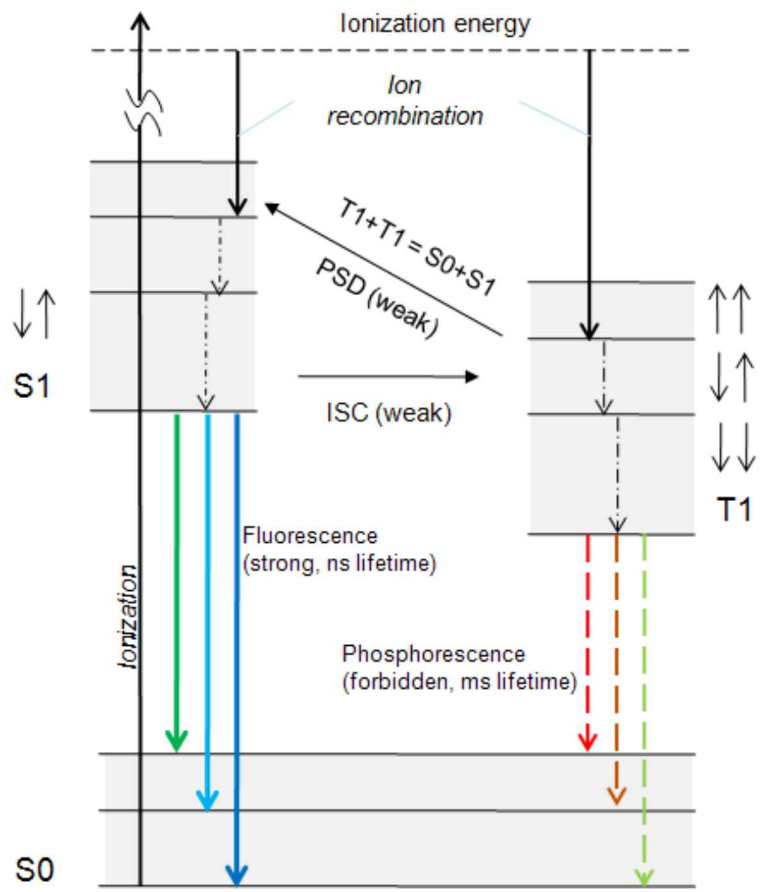
CC3

D. Banerjee et al. *Chem.* 4 (2018), 466–494

Basics of radiation detection using organic scintillators

Typical luminescent MOF linkers have fused aromatic rings



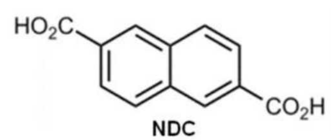


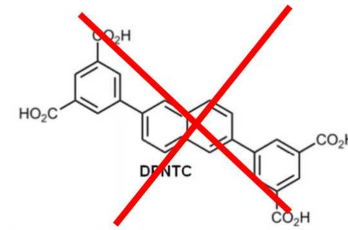
Design principles for MOF-Based Scintillators

- Use closed-shell metal cations
  - E.g., Zn or Cd
  - No MOFs with open metal sites

$Zn_4O(O_2CR)_6$

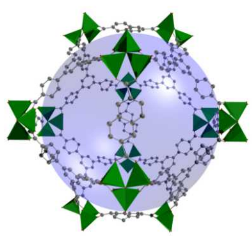
- Avoid non-rigid linkers with non-radiative pathways



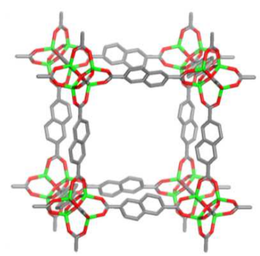


- Adopt rigid framework topologies

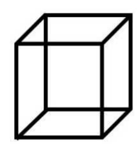
- Electronically isolate linkers

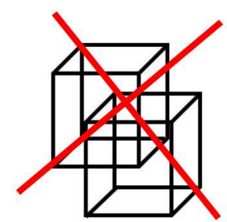


DUT-6



IRMOF-8

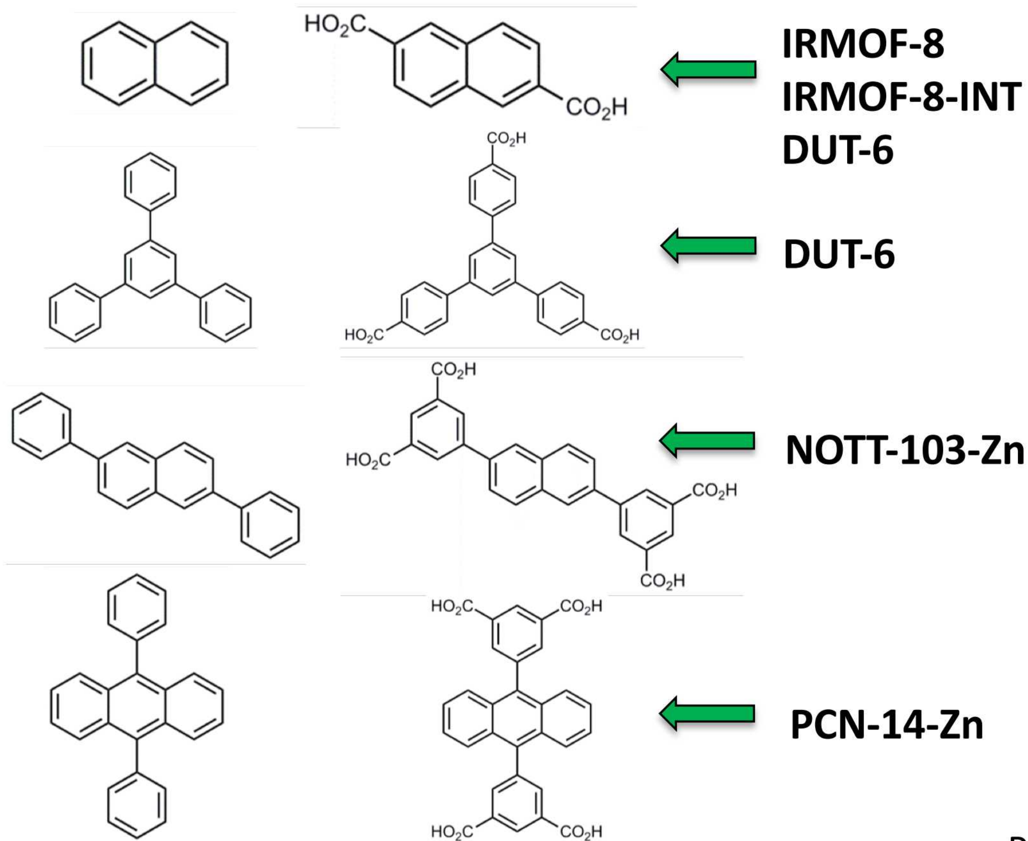




We are characterizing the radio-luminescent and gas sorption properties of several candidate MOFs

Systematic tailoring of MOF radioluminescence is feasible

Molecular Scintillator | **MOF Organic Linker** | **MOF Scintillator**



MOF	Light yield*
DUT-6	79%
IRMOF-8	124%
IRMOF-8-INT	55%
NOTT-103-Zn	64%
PCN-14-Zn	39%

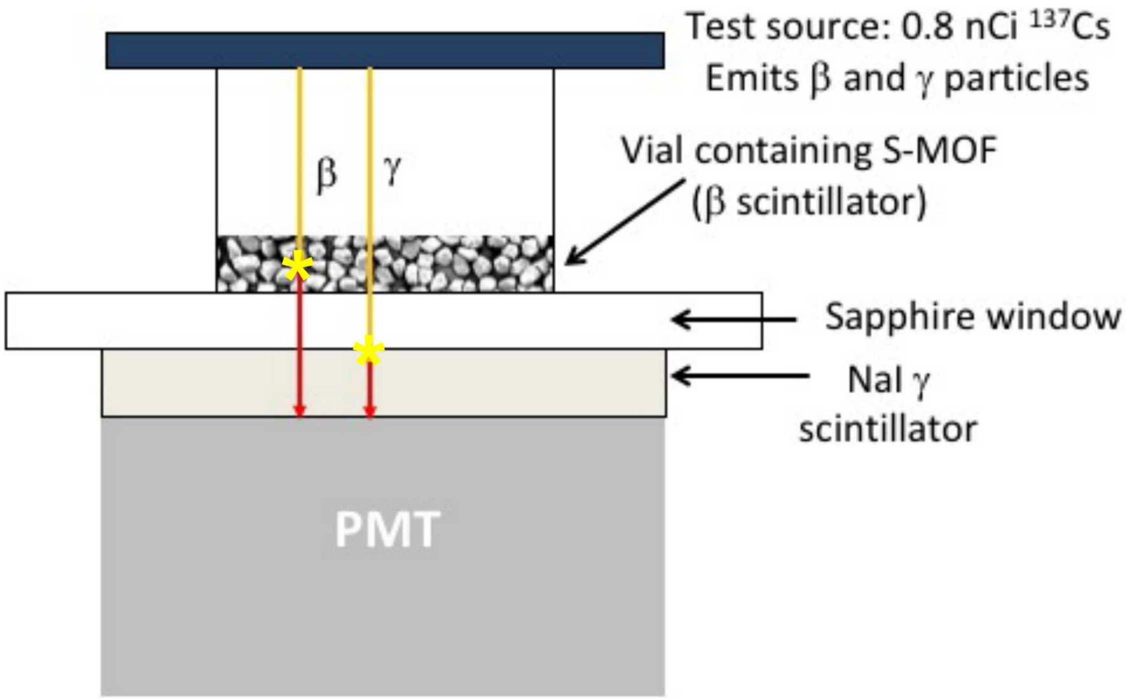
*Relative to *trans*-Stilbene

Light Yield: Linker-based luminescence is at least as bright as the analogous molecular scintillator

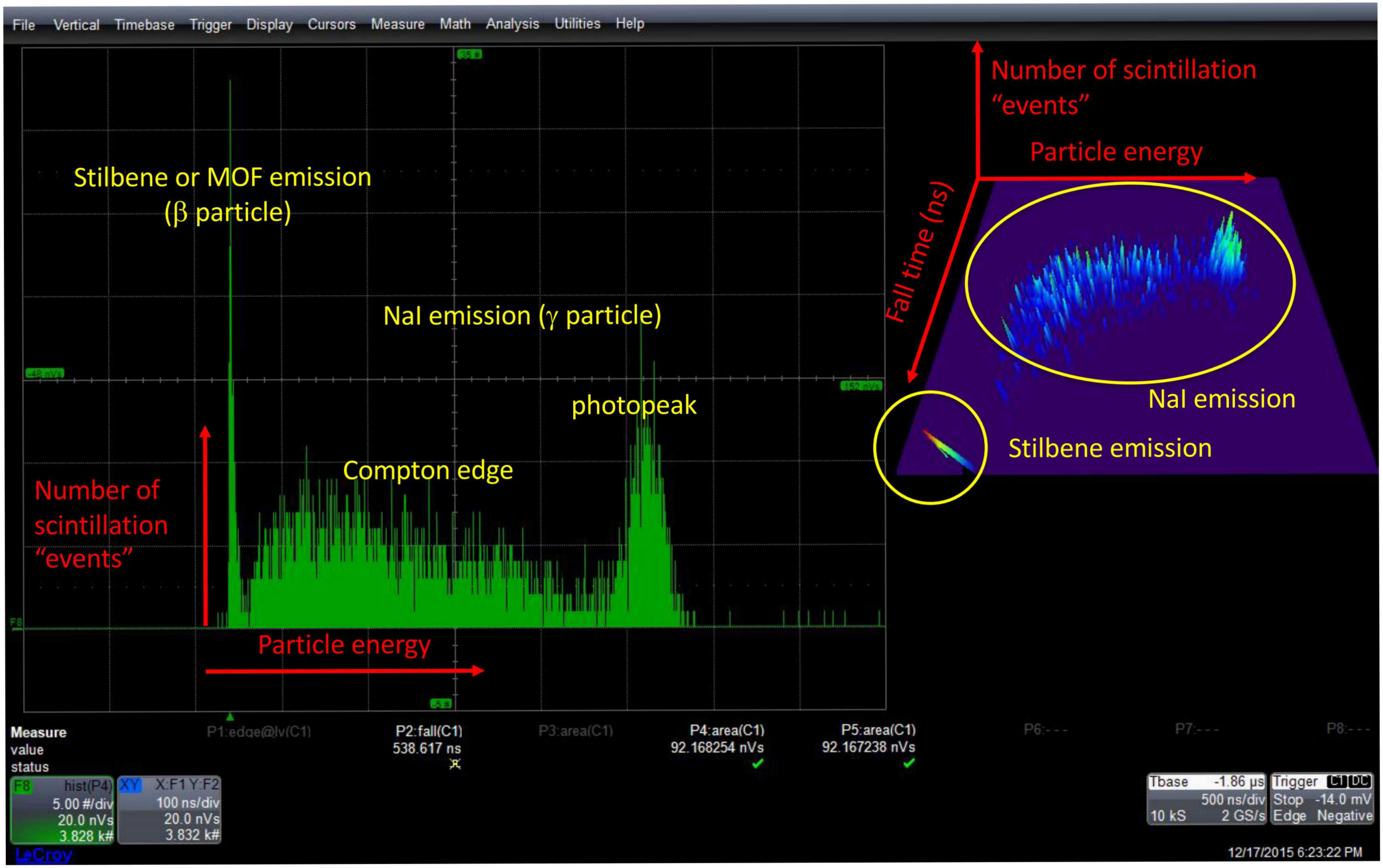
Perry IV, J.J. *et al., J. Mater. Chem.* **2012,** *22*(20), 10235

“Phoswich detector” for evaluating S-MOFs

- **Use to determine ability of S-MOF to distinguish between particle types**
- **Addition practical value: discriminate against background γ and muons**



Phoswich two-parameter histogram: stilbene reference powder



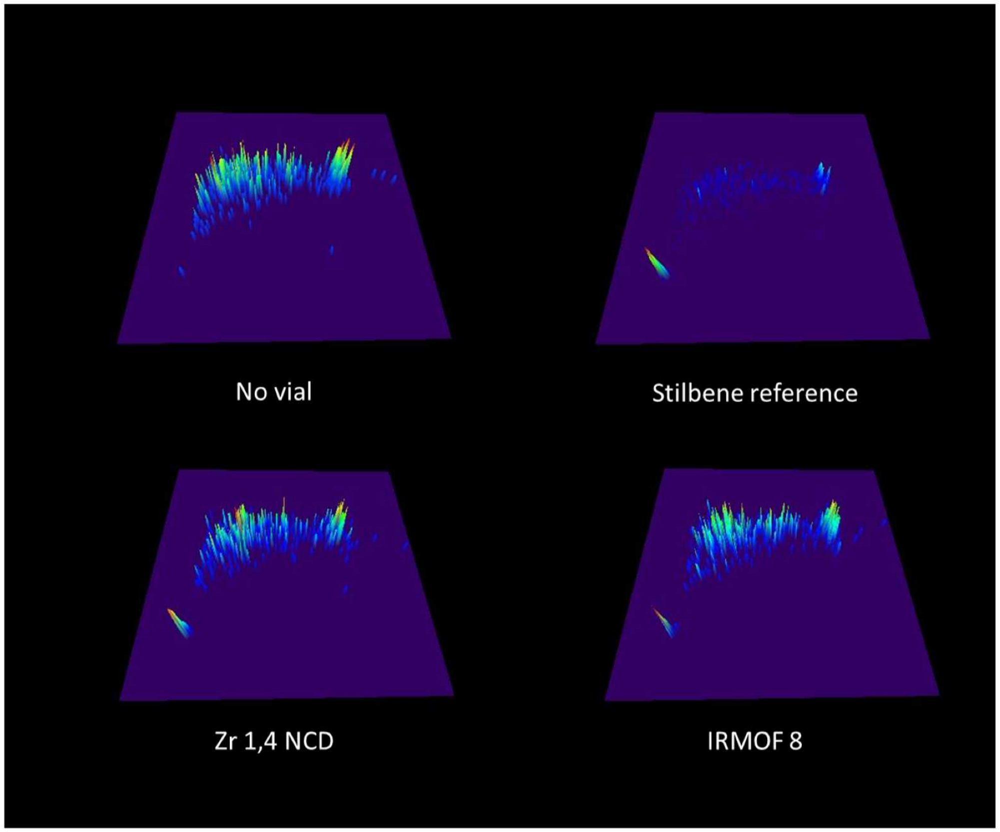
Scintillating MOFs in phoswich detector prototype

- **Prototype dual-phoswich detector design**
  - –Powder bed with pressure window
  - –Two γ scintillators/PMTs (NaI:Tl)

- **Demonstrated viability of detection**
  - –Photons detected/unit absorbed β energy
  - –Source: 0.8 nCi ^{137}Cs β/γ 4 cm above MOF

- **NaI and MOF pulses are clearly separated**
  - →Fast MOF phosphors can be used as a β trigger in a phoswich detector

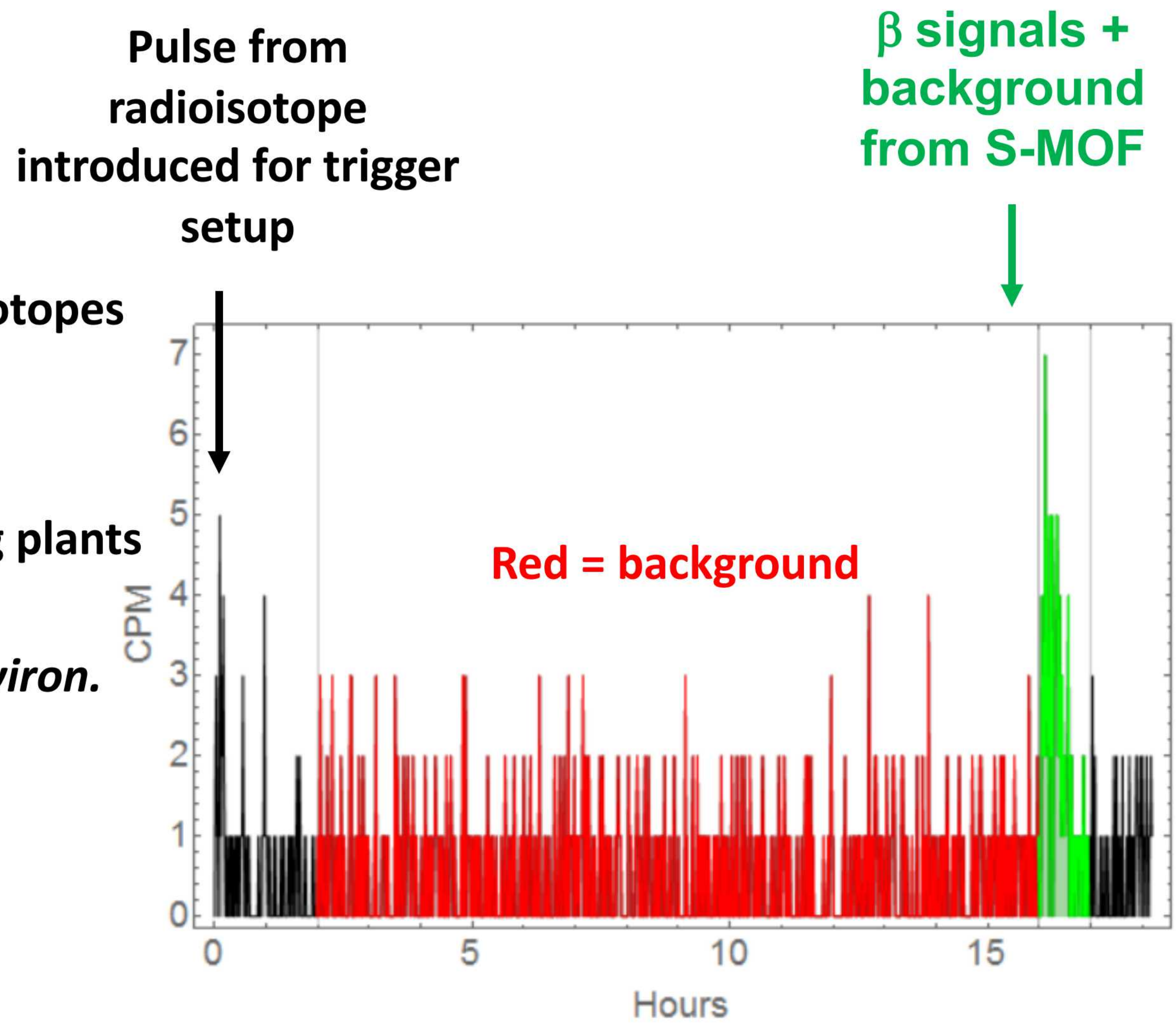
- **Figure of Merit (FOM) determined using stilbene reference**
  - –130 photons/MeV from fast electrons
  - –FOM is 43 photons/MeV/ns assuming 3 ns radioluminescence decay time



Detection of β particles from a noble gas isotope using Zr(1,4-naphthalene dicarboxylate) as S-MOF

^{85}Kr as surrogate for short-lived Xe isotopes

- Half life 10.8 years
- ~ 1 ppm Bq/m^3 in air
- Source is nuclear fuel reprocessing plants in the Northern Hemisphere
    - e.g. see Y. Igarashi et al. *J. Environ. Radioactivity* 48 (2000) 191



S:background determined to be 8σ at 1 bar pressure, sufficient to detect the isotope

Conclusions

- **MOFs possess a unique combination of properties that make them useful for detecting noble gas isotopes**
  - **Scintillation**
  - **Selective uptake over majority atmospheric components**
- **Detection of β and γ particles was demonstrated using a surrogate for short-lived Xe isotopes**

→ S-MOFs show potential to replace conventional porous carbons and allow rapid detection of trace gases resulting from nuclear detonations

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- GCMC simulations and MOF screening
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- MOF consolidation
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