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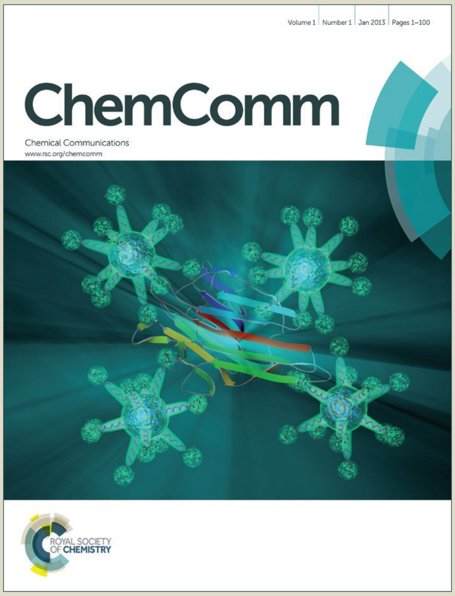

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Stability of Metal-Organic Frameworks under gamma irradiation

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We report the study of the resistance of archetypal MOFs (MILs, HKUST-1, UiO-66, ZIF-8) under gamma irradiation. The different porous solids were irradiated to dose up to 1.75 MGy. All the MOFs constructed with transition metals (Cu^{2+}, Zn^{2+}, Zr^{4+}) exhibit an evident destruction of the framework, whereas the compounds inserting aluminium remain intact.

Since their discovery, hybrid crystallized porous materials so-called Metal-Organic Framework (MOF), are very promising materials to solve societal issues. Indeed, the remarkable porosity of this class of solids is currently exploited for the capture of strategic gases (H_2, CO_2, CH_4, noble gases, etc.), drug release, catalysis and many other applications.[1]

The interest of MOFs in nuclear applications arises after the Fukushima disaster. At that time, porous materials have already been considered by the nuclear industry for the capture of radionuclides during nuclear processes or in the case of an industrial accident. For example, purely-inorganic zeolites can be used for the adsorption of gaseous iodine (mainly silver doped zeolites) and for the capture of cations in radioactive solution. Activated charcoals are also quite efficient for volatile radio-iodine removal and for trapping, in environmental samplers, airborne iodine derivatives liberated by nuclear plants.[2]

So far, the studies involving the adsorption of gaseous radionuclides (I_2, Xe, Kr)[3-5] in MOFs have shown very high uptakes and opened opportunities for radionuclides separation and long-term immobilization. The immobilization of solubilized radioactive species in MOFs concerns only uranyl cations and indicates adsorption capacity comparable to those observed with functionalized mesoporous silica (200-300 mg of $[UO_2]^{2+}$ per gram of adsorbent).[6, 7]

The different studies dedicated to the capture of radionuclides in MOFs led to very promising results. However, many queries remain before the utilization of MOFs for the capture of radiotoxic molecules during a nuclear accident or other processes involving radioactive species, like gas treatment[2, 4], medicine[8] or scintillation materials.[9-12] One of the main questions concerns the resistance of MOF under ionizing radiation generated by radioactive decay. This aspect is rarely studied in hybrid organic-inorganic compounds although some contributions described the stability of Zr/Sn phosphonates materials under gamma ray[13] or Hf/Zr MOFs under X-ray have been mentioned.[14]

Due to their lower ionizing power than alpha and beta particles, gamma rays are more penetrating: they provide the easiest alternative for investigating the radiation damage on materials.

In this study, we analysed the effect of gamma irradiation of different MOFs in order to determine their resistance under strong ionizing radiation. For a better overview, the selected MOFs (ZIF-8,[15] HKUST-1,[16] MILs,[17] UiO-66[18]) involves different metals and oxidation degrees (Zn^{2+}, Cu^{2+}, Al^{3+}, Zr^{4+}), porosities and correspond to prototypical MOFs widely studied in the literature, especially in the case of radionuclides sorption.[5, 6, 19-21] Other archetypal MOFs, such as MOF-5, were not selected due to their very low stability under air.[22]

The different porous solids were submitted to different doses in the range 0.5 - 2 MGy, within the gamma irradiation cell called IRMA – IRradiation MAterials – (Figure S4) of the Institute of Radiological Protection and Nuclear Safety (IRSN) at Saclay Research Center. This irradiation cell is equipped with several ^{60}Co sources and the dose rates applied for this study were between 2 and 5 kGy/h. Dosimetry was performed using a calibrated ionization chamber on each MOF tested in the irradiation cell.

The solids were synthesized and activated following published procedures from literature. After gamma irradiation, the solids were characterized by means of different techniques (PXRD,

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†Electronic Supplementary Information (ESI) available: Synthesis procedures, gamma ray installation and analytical data: powder XRD patterns, BET curves, photos, NMR spectra, IR spectra. See DOI: 10.1039/x0xx00000x

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infrared, N_2 sorption, NMR) in order to define the effect of irradiation and the robustness of the framework.

The first study was carried out with ZIF-8 (imidazolate zinc-based MOF), due to its interest in iodine capture.[3] The powder X-ray diffraction diagrams of ZIF-8 samples irradiated at 0.5, 0.75 and 1 MGy, are quite similar to the reference. However higher irradiation doses (between 1.25 and 1.75 MGy) gave rise to the observation of broader Bragg peaks (Figure 1 and Figure S5g) together with lower intensities, indicating an important loss of crystallinity.

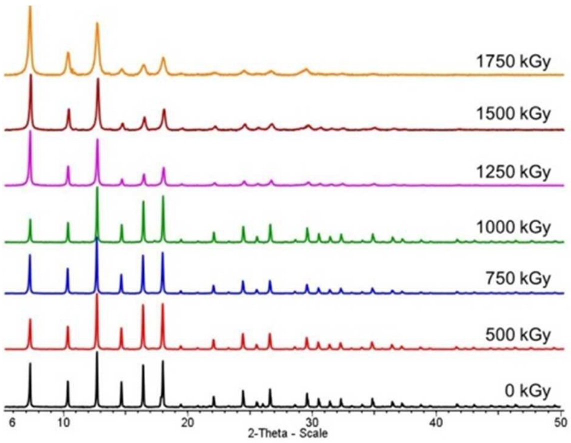

Figure 1. Evolution of powder X-ray diffraction patterns of non-irradiated and gamma irradiated zinc-based compound MOF ZIF-8 (copper wavelength) at different doses (0-1.75 MGy)

Whereas PXRD technique gives an averaged picture of the irradiated framework, Nuclear Magnetic Resonance (NMR) is more informative about the local defects created by the irradiation. The ^{13}C NMR spectrum of ZIF-8 (Figure S8a) shows three peaks at 151.2, 124.2 and 13.7 ppm, assigned to the carbon atoms of the imidazolate ligand organizing the porous framework. After a dose of 1.75 MGy, all these peaks become broader and we note the appearance of several new resonances at 170.5, 146.7, 117.7, 51.9, 14.9 and 11.9 ppm. Similar behaviour is also observable for the ^{15}N NMR spectrum (Figure S8b).

The NMR signature of the irradiated material indicates structural transformation that could be explained by major structural distortion (resonances at 170.5, 14.9 and 11.9 ppm) and/or the breaking of chemical bonds, leading to the presence of free ligand in the pores (signals at 146.7, 117.7, 51.9 ppm). This last explanation is well supported by nitrogen sorption at 77K, which shows an important loss of porosity (Figure 2). Whereas the non-irradiated ZIF-8 solid exhibits a relative high porosity (saturation at 360 cm^3 of N2 per gram of MOF), the irradiated solids have much less affinity for nitrogen at 77K (325-160 $cm^3.g^{-1}$). This decrease is directly linked to the irradiation process, which induces a lower porosity when increasing the gamma dose. For a dose of 1.75 MGy, irradiated ZIF-8 is characterized by a BET surface of 598 $m^2.g^{-1}$ (microporous volume of 0.198 $cm^3.g^{-1}$) which is approximately half as much of the non-irradiated solid (BET of 1328 $m^2.g^{-1}$ and microporous volume of 0.545 $cm^3.g^{-1}$), synthesized from the same batch (Figure 2).

Other MOFs solids have been tested such as UiO-66 and HKUST-1 (Zr-and Cu-based MOFs, respectively). The different structural characterization show that they are also quite sensitive to the gamma irradiation dose and exhibit a similar behaviour than ZIF-8. Although the destruction of these MOFs is less marked by PXRD or infrared than for ZIF-8, the decomposition of their structure after an irradiation of 1.75 MGy is confirmed by the loss of porosity of approximately 30%, as compared to the initial MOF (See supporting information).

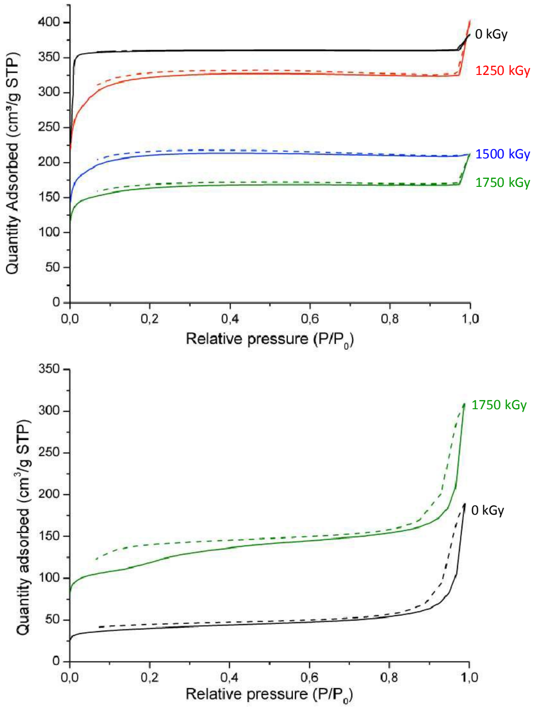

Figure 2. Isotherm curves for the adsorption (solid) and desorption (dash) of nitrogen (77K) in irradiated and non-irradiated ZIF-8 (top) and MIL-120 (bottom)

Then three other MOFs compounds bearing aluminium (MIL-53, MIL-100, MIL-120) exhibit a better stability. Whatever the gamma dose (up to 1.75 MGy), X-ray diffraction, NMR or IR techniques do not indicate any signs of structural decomposition or framework collapsing. In the case of MIL-53, the porosity is not affected by the gamma radiation and we do not observe any modification of the framework swelling of the structure. The influence of radiation on the porous solid is quite more pronounced in the case of MIL-100. Surprisingly, we observe a slight elevation of the quantity of nitrogen adsorbed in the pores (Figure 2), corresponding to a gain of BET surface value of 215 m²/g (11%). In the case of MIL-120(Al), this difference is even more important, with an increase of the specific surface of 190% (273 m²/g). For both

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solids, this improvement of the porosity, without any structural modification, is assigned to the removal of species trapped within the pores and limiting the accessibility of the probe molecule. Such poisoning molecules are assigned to fragment of trimesate ligand or dimethylformamide in the case of MIL-100.[23, 24] The decomposition of extra-framework non-bonded organic molecules by gamma irradiation is even more pronounced for non-chemically/thermally activated solids, such as as-synthesized MIL-100(Al) (notes MIL-100(Al)-as) (Figure 3). After synthesis, this solid is characterized by a relative low BET value (858 m^2/g), mainly due to unreacted trimesic acid molecules trapped into the pores, easily identifiable by IR spectroscopy (shoulder at 1720 cm^{-1}) (Figure S7d). The dose of irradiation received by non-activated MIL-100 (up to 2000 kGy), induces a constant elevation of the accessible porosity, up to a maximum of 1959 m^2/g (BET model) for an irradiation of 2000 kGy (Figure 3). This change coincides with the departure of free trimesic acid, which is confirmed by infrared (disappearance of the band at 1720 cm^{-1})[23] (Figure S7d). This last study corresponds to the highest irradiation dose received by a MOF and confirms the remarkable stability of MIL-100(Al). For information, such dose corresponds to the exposure received by filter localized for 8 days in the reactor building during a nuclear accident.[25]

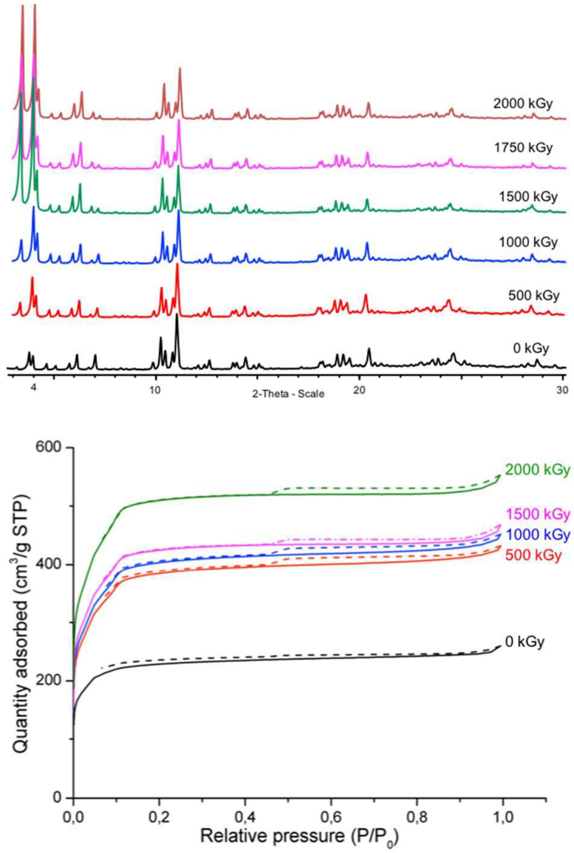

Figure 3. Influence of gamma irradiation doses (0-2 MGy) over as-synthesized MIL-100(Al): (bottom) Isotherm curves for the adsorption (solid) and desorption (dash) of nitrogen (77 K). (top) Powder X-ray diffractograms

In the infinite library of Metal-Organic Frameworks, it appears that the resistance of the solid is mainly dependent on the strength of the interaction between the metallic cations and the organic ligand. Based on the HSAB (hard and soft acids and bases) concept, the association of hard Lewis acid (metallic cation) and base (organic linker) induces a strong interaction, resulting in a relative good stability versus chemical attack or temperature. This explains why MOF constructed from hard Lewis acids such as trivalent aluminium or tetravalent zirconium and carboxylate ligands are generally considered as the most stable MOFs. For example, MIL-53(Al) and UiO-66(Zr) are the most thermally stable (500°C under air)[18, 26], and exhibit a rather good resistance versus hydrolysis.[27] On the other hand, divalent metals based (softer Lewis acid) exhibit a lower stability, which is well highlighted by the quick decomposition of many compounds just under air.[22]

As indicated in this study, the radiolytic stability of MOF under gamma irradiation is not directly related to the Pearson acid base concept, but follows another trend. This tendency is not based on the ligand since aluminium terephthalate (MIL-53) and trimesate (MIL-100), are quite stable, whereas their analogues with zirconium (UiO-66) and copper (HKUST-1) are damaged.

The interaction of the highly penetrating gamma radiation with matter is proportional to the absorption cross section and the density of the material. Whereas the organic constitution and the density of the examined MOFs are quite similar, the main difference relies on the nature of metal utilized for their synthesis. The probability of beam to interact with a metal is governed by the cross section of the latter one (see supplementary information). This interaction can be modulated by the number of metal atoms in the MOF structure and the void space in the structure.

The determination of the cross-section of the metals forming the MOF employed in this study, was realized using NIST-XCOM database[28] and calculated for ^{60}Co energies (Table Sx).

The calculated values (Table S1) indicate a gap between aluminium (2.5 barns/atom) and the transition metals (>5.3 barns/atom). This result implies a lower gamma ray absorption of MOF constructed with aluminium than those synthesized with copper, zinc or zirconium. Due to the relative low interaction of Al-based MOF with gamma ray, no effect of this radiation is observable for doses up to 1,75 MGy. In the case of metal showing higher likelihood of absorption of gamma ray, the radiation interaction with the inorganic sub-network is transferred to the organic part. This role of metal-oxo cluster in MOF as radiation antenna was already mentioned by Lin for the use of anthracene-based UiO-n solids as X-ray scintillators.[14]

This phenomenon makes easier the degradation of the connected ligand through radiolysis mechanisms, involving the formation of ions, excitons and organic radicals. The particular low stability of ZIF-8 versus gamma irradiation would be accentuated by the presence of an aliphatic component (-Methyl), which is more sensitive than aromatic rings, to gamma irradiation.[29, 30] Whereas the crystallized framework Al-based MOFs remain stable under gamma irradiation (at least

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up to 2 MGy), impurities trapped within the pores are directly impacted by the gamma photons. Such sensibility could be explained by strong interaction between metallic centers (gamma rays antenna) and impurities localized in the pores. For MIL-100, this affinity was already mentioned in the literature, explaining the difficulty to activate this solid.[23, 24]

In summary, we have demonstrated the high resistance of aluminium-based MOF under gamma irradiation (comparable to at least 8 days under strong radioactive conditions during a nuclear accident), compared to similar materials synthesized with transitions metals, HKUST-1(Cu), UiO-66(Zr) and ZIF-8(Zn). This stability is assigned to the lower cross section of aluminium, limiting the effect of gamma ray and the destruction of the hybrid framework. Whereas the porous network preserves its integrity in the case of Al-MOFs, organic molecular fragments inserted in the pores are more sensitive to irradiation. This embrittlement leads to a partial removal of this species and increase the available porosity of the material. These results confirm the great potential of MOFs, especially those constructed with aluminium, in the case of nuclear accident. However, this significant tolerability gives also obvious opportunity for other industrial fields involving radiation environments (such as gamma rays), as for example in medicine or aerospace.

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