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**LUMINESCENT MOFs ARCHITECTURES FOR RADIOACTIVE GAS DETECTION AND ENGINEERING LARGE STOKES SHIFT**J. Perego,<sup>a</sup> C. X. Bezuidenhout,<sup>a</sup> S. Bracco,<sup>a</sup> F. Cova,<sup>a</sup> M. Orfano,<sup>a</sup> S. Piva,<sup>a</sup> B. Sabot,<sup>b</sup>  
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The precise spatial assembly of chromophores inside MOF allows for the rational fabrication of photonic materials with unique photophysical properties. We propose an innovative radioactive gas detector based on highly porous luminescent MOFs.<sup>[1]</sup> Hf-based MOFs containing diphenyl anthracene (DPA) moieties display high porosity ( $S_{\text{BET}} = 2550 \text{ m}^2 \text{ g}^{-1}$ ), fast and reversible adsorption of noble gases (proven by combined experimental adsorption and simulation methods) and high photoluminescence and scintillating properties. After exposure to radioactive gases, Hf-DPA displays fast and bright scintillation sensitized by the decay of the radioactive nuclei that allows for their effective detection at ultra-low concentrations. Indeed,  $^{85}\text{Kr}$  isotope was detected even at activity as low as  $0.3 \text{ kBq}\cdot\text{m}^3$ , below the minimum value declared for commercial devices, strongly supporting the development of MOF-based scintillators for radioactive gas detection.

Fast composite scintillators were engineered by embedding nanocrystalline Zr-MOFs containing highly luminescent DPA moieties in a continuous polymer matrix.<sup>[2]</sup> The hybrid bulk scintillators display good light yield, fast time response and an ultrafast scintillation rise time of  $\sim 50 \text{ ps}$ , making them promising materials for time resolved applications. Moreover, nanocrystalline hetero-ligand Zr-based MOFs with high luminescent quantum yield and large Stokes shift emission were engineered by co-assembly donor and acceptor chromophores, diphenyl anthracene (DPA) and diphenyl tetracene (DPT) moieties, respectively, to generate reabsorption-free emitters with potential applications in bio-imaging, solar luminescent concentrators and bulk scintillators.<sup>[3]</sup> The two luminescent ligands, with similar molecular length and topology, were homogeneously inserted inside the MOF nanocrystals as proven by  $^{129}\text{Xe}$  hyperpolarized NMR experiments. The overlap between the emission frequency of DPA molecule and the absorption spectrum of DPT, and the precise spatial arrangement of neighbor chromophores promote fast energy diffusion and effective energy transfer inside the MOF nanocrystals, generating large Stokes shift emission ( $\Delta E \sim 6000 \text{ cm}^{-1}$ ) with fluorescence quantum yield of  $\sim 0.6$ . The remarkable photophysical properties of these large Stokes shift emitters stimulate the preparation of fast emitting composite scintillators with negligible reabsorption and benchmark performance comparable to commercial materials.

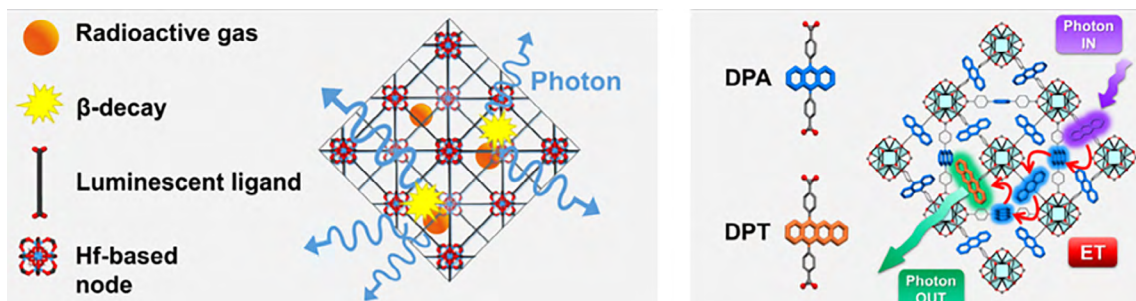


Figure 1. Scintillating MOFs for radioactive gas detection (left) and large Stokes shift luminescent MOFs designed for fast and reabsorption-free scintillators (right).

**References**

- [1] M. Orfano, J. Perego et al. *Nature Photonics* **2023**, in press.
- [2] J. Perego, et al. *Nature Photonics* **2021**, 15, 393-400.
- [3] J. Perego, et al. *Nature Communications* **2022**, 13, 3504.