

Re-absorption free scintillating MOFs crystals activated by ultrafast energy transfer.

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Limiting the self-absorption of the luminescence emission to maximize the light output is crucial in bulk photonic devices, especially in the case of the luminescent scintillators employed to monitor the ionizing radiations. Unfortunately, large Stokes shift materials, such as phosphorescent chromophores or electronically-doped semiconductor nanocrystals, often show slow emission rates which hinders their use if fast emitters are required to get high quality images in short times, such as in biomedical imaging, or to avoid detrimental pile-up of the recorded emitted photons, such as in high-rate/high-energy events or for the detection and activity quantification of gas radionuclides. [1]

To overcome this limitation, we demonstrated that fast scintillation with large Stokes shift can be obtained in metal-organic frameworks (MOF) crystals engineered with inorganic linking nodes containing heavy elements prone to interact with the ionizing radiations and highly fluorescent conjugated ligands. [2][3] We realized hetero-ligand MOFs with a Stokes shift as large as 1 eV, thus completely eliminating the self-absorption issue, by co-assembly of scintillating ligands with complementary emission and absorption properties. Importantly, the specific electronic properties of the conjugated ligands allow the sensitization of emissive ligands by means of an ultrafast diffusion-mediated non-radiative energy transfers with a rate up to the THz range. This extremely efficient mechanism enables to instantaneously active the ns-lifetime scintillation emission of MOF crystals. The efficient antenna mechanism, and the consequent elimination of reabsorption, enables to preserve the structural and gas adsorption properties of the parent homo-ligands MOF surpassing by 500% its scintillation yield. In the optimal composition, the hetero-ligand MOF has been tested to capture and detect the radioactive krypton isotope ⁸⁵Kr in the gas phase, demonstrating a high affinity for this radionuclide and an improved detection sensitivity with respect to the reference homo-molecular system. [4]

1. Orfano, M.; Perego, J.; et al. *Nature Photonics* **17**, 672- 678 (2023).
2. Perego, J.; Villa, I. et al. *Nature Photonics* **15**, 15, 393-400 (2021).
3. Perego, J.; Bezuidenhout, Charl X.; et al. *Nature Communications* **13**, 3504 (2022).
4. Orfano, M.; Perego, J.; *in preparation* (2024)

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