Highly luminescent hetero-ligand MOF Nanocrystals with Engineered Stokes shift for Photonics Applications.

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The Stokes shift is an important property of luminescent materials, defined as the energy difference between the absorption band maximum and the emission spectrum maximum frequencies. Its extent crucial in photonic devices because it enables to estimate in a first approximation if a specific emitter would be affected by reabsorption of its luminescence. If the Stokes shift is lower or similar to the bandwidth of the absorption and emission spectra, the consequent '*inner-filter'* effect can heavily limit the lighting performance of bulk devices, and, in the worst cases, it can also affect the kinetics of the luminescence generation. Conversely, if the Stokes shift is larger than the system spectral bandwidths this effect is avoided. Thus, reabsorption-free materials are highly desirable for several applications such as fluorescence imaging, enabling to obtain high contrast images with limited excitation stray light, avoiding the use of expensive filtering component or time-consuming image post-processing. For solar applications, to realize luminescent solar concentrators without reabsorption of the condensed radiation. Similarly, the sensitivity of scintillating detectors for ionizing radiation would greatly benefit from the use of fast emitters with no reabsorption showing maximum light output intensity without effects on the scintillation pulse timing, as required by the most advanced medical imaging, sensing and metrology techniques. [1]

High efficiency, large Stokes shift emission is obtained by realizing *hetero*-ligand Metal-Organic Framework (MOF) nanocrystals. Two fluorescent conjugated polyacene ligands of equal molecular length and connectivity, yet complementary photophysical properties, are co-assembled by zirconium oxy-hydroxy clusters, generating highly crystalline MOF nanoparticles. The fast diffusion of singlet molecular excitons in the framework, coupled to the achieved fine matching of co-ligands absorption and emission properties, enables to achieve an ultrafast activation of the low energy emitting ligands by diffusion-mediated, non-radiative energy transfer in the 100 ps time scale. In the optimized composition, MOF nanocrystals show a fluorescence quantum efficiency of ~ 70% with an actual Stokes shift of 750 meV. This large Stokes shift suppresses the reabsorption of fast emission issue in bulk devices, pivotal for a plethora of applications in photonics and photon managing spacing from solar technologies, imaging, and detection of high energy radiation. These features allowed to realize a prototypal fast nanocomposite scintillators that shows an enhanced performance with respect to the *homo*-ligand nanocrystals, [2] achieving benchmark values competing with those of some commercial inorganic and organic systems.

[1] Orfano, M., et al. *Nature Photonics* **17**, 672–678 (2023)
[2] Perego, J., et al. *Nature Communications* **13**, 3504 (2022)