Ultra-Fast Rotors and Light Emitting Ligands in Metal-Organic Frameworks

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Rotors, motors and switches in the solid state find a favorable playground in porous materials, such as Metal Organic Frameworks (MOFs), thanks to their large free volume, which allows for fast dynamics. We fabricated MOFs with reorientable linkers and benchmark mobility also at very low temperature, to reduce the energy demand for motion-activation and light stimulus-response.

In particular, we have realized a fast molecular rotor in the solid state whose rotation speed approaches that of unhindered rotations in organic moieties even at very low temperatures (2 K). The rotors were hosted within the struts of a low-density porous crystalline MOF and energetically decoupled from their surroundings. A key point was the unusual crossed conformation adopted by the carboxylates around the pivotal bond on the rotor axle, generating geometrical frustration and very shallow wells along the circular trajectory. Continuos, unidirectional hyperfast rotation with an energy barrier of 6.2 cal/mol and a high frequency persistent for several turns is achieved (10 GHz below 2 K).[1]

Responsive porous switchable framework materials endowed with light-responsive overcrowded olefins, took advantage of both the quantitative photoisomerization in the solid state and the porosity of the framework to reversibly modulate the gas adsorption in response to light. [2]

Motors were inserted into metal-organic frameworks wherein two linkers with complementary absorption-emission properties were integrated into the same materials. Therefore, unidirectional motion was achieved by simple exposure to sun-light of the solid particles, which thus behave as autonomous nanodevices.[3]

MOF nanocrystals comprising high-Z linking nodes interacting with the ionizing radiation, arranged in an orderly fashion at a nanometric distance from diphenylanthracene ligand emitters showed ultrafast sensitization of the ligand fluorescence, thus supporting the development of new engineered scintillators.[4]



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