

*Flexible and phosphorescence Cu(I) triazolate MOFs for optical oxygen sensing*Si-Yang Liu<sup>1</sup>, Jie-Peng Zhang<sup>1</sup>, Xiao-Ming Chen<sup>1</sup><sup>1</sup>School Of Chemistry, Sun Yat-Sen University, Guangzhou, China

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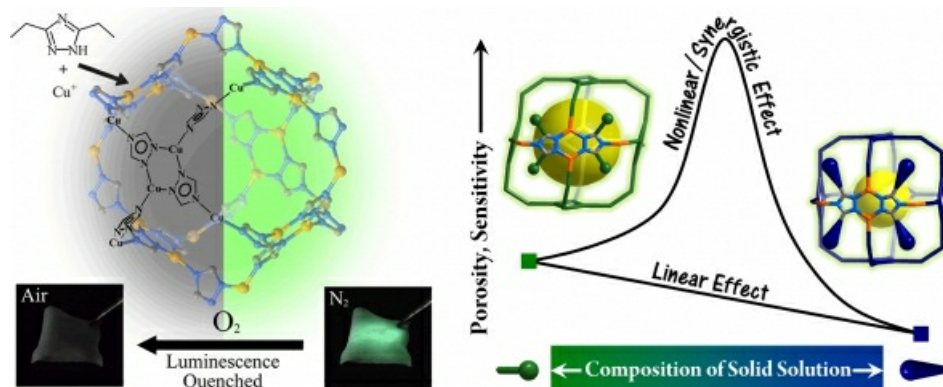
Metal-Organic Frameworks (MOFs) is a novel porous material constructed by organic ligands and metal ions through coordination bond, therefore, utilizing ligand/metal ions with similar coordination geometry to construct solid solutions is so far one of the most efficient method to modify the properties of MOFs. As a material possessing both the order of crystal and the disorder of mixture, the solid solutions commonly belong to the same structure as their parent phases, and exhibiting intermediate properties in-between their parent phases. Theoretically, rational design of multiple building blocks may result in synergistic effect and improve the properties of solid solutions, even better than the parent phases.

Recently, the MOF-based oxygen sensor has drawn great attention for its designability and porous nature. And oxygen sensing is widely applied in biology, medicine, chemical industry, etc with different detection range requirements. Our group has established several Metal-Azolate Framework (MAF) based materials, which contain small amount noble metal or are noble-metal-free, for optical oxygen sensing. Among them, flexible and porous MAF-2 (Cu(I) 3,5-diethyl-1,2,4-triazolate) exhibit the highest oxygen sensitivity (KSV = 356 bar<sup>-1</sup>, limit of detection (LOD) = 28 ppm) in MOF-based materials at that time. Besides, due to the facile synthesis of MAF-2, an in-situ diffusion crystal growth method was developed to hybrid silicon rubber with MAF-2 for flexible oxygen membrane sensor.[1]

In order to obtain various oxygen sensitivity for the greatly distinguished sensitivity requirements in practical applications, we introduced both smaller and larger side groups (methyl, propyl, butyl) into MAF-2 backbone. Due to the flexibility of MAF-2 and the similarity of the non-isostructural framework of the corresponding ligands, the crystal structure of solid solution frameworks transform along with the ratio and component of ligands between three crystal systems. More interestingly, near the phase boundaries, the porosity (+150 %) and optical oxygen sensitivity (410 times, LOD = 0.07 ppm) can be drastically improved from the best-performing parent MOFs and even exceeds the records hold by precious-metal complexes (3 ppm) and C70 (0.2 ppm). In addition, a suitable low sensitivity for ambient oxygen sensing (~ 21% atm) can also be achieved. Generally speaking, these solid solution frameworks cover 8 orders of magnitudes in detection range for oxygen sensing (0.07 ppm to ~ 1 atm), which meet basically all the requirements for detection range in oxygen sensing.[2]

[1] Liu, S.-Y. et al. (2014). *Adv. Funct. Mater.*, 24, 5866–5872.

[2] Liu, S.-Y. et al. (2016). *Angew. Chem. Int. Ed.*, 55, 16021-16025.



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