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Title: Subtle Ligand Spacer Change in 2D Metal-Organic Framework Sheets for Dual Turn-On/Turn-Off

Sensing of Acetylacetone and Turn-On Sensing of Water in Organic Solvents

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Subtle Ligand Spacer Change in 2D Keywords:

Sensing of Acetylacetone

Sensing of Water in Organic Solvents

Issue Date: 2022

Publisher: **ACS Publications**

Citation: ACS Applied Materials and Interfaces, 14(14), 16357-16368.

Abstract:

Metal-organic framework (MOF)-based sensors for the detection of various analyte molecules has been a subject of absolute importance. However, most of these sensors rely on the turn-off (quenching) transduction response, while those reporting turn-on response are very rare. In this article, we have synthesized two new MOF-based sensors, {[Zn2(oxdz)2(tpbn)]·14H2O}n (1) and {[Zn2(oxdz)2(tpxn)]·10H2O·2C2H5OH}n (2), via the self-assembly of Zn(II) metal ions, a fluorogenic oxdz2- linker, and bis(tridentate) ligands (tpbn and tpxn) under ambient conditions. Their formation from such a self-assembly process has been evaluated on the basis of the geometry around the five-coordinated Zn(II), preferential meridional binding of the bis(tridentate) ligands, and diverse binding of the carboxylate groups in oxdz2-. Although 1 and 2 are isostructural, a difference in the transduction mechanism for the sensing of acetylacetone in organic solvents (turn-on for 1 and turn-off for 2) is observed and can be attributed to the spacer in the bis(tridentate) ligands. We have demonstrated the competing effect of the nonradiative interactions and photoinduced electron transfer toward the sensing mechanism. The results are well-supported by the Fourier transform infrared spectroscopy study, intensity versus concentration plots, spectral overlap measurements, time-resolved fluorescence studies, and MM2 and density functional theory calculations. Furthermore, we have showcased the utilization of 1 for the sensing of trace amounts of water in organic solvents.

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URI: https://doi.org/10.1021/acsami.2c02798 (https://doi.org/10.1021/acsami.2c02798)

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