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Theoretical Insights into the Luminescence Mechanism of a Metal-Organic Framework (MOF) Chemosensor Selective to Alkylamines

Yoan Hidalgo Rosa[a], Manuel A. Treto Suárez[a], Dayan Páez-Hernández[a], Ximena Zarate[b,c*]*

[a]Doctorado en Fisicoquímica Molecular, Center of Applied Nanosciences (CENAP), Universidad Andrés Bello. Ave. República #275, Santiago de Chile, Chile. d.paezhernandez@yahoo.es;yoanhrj@gmail.com.
[b]Instituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, Av. Pedro de Valdivia 425, Santiago, Chile. jazminac@gmail.com.
[c]Millenium Nuclei on Catalytic Processes towards Sustainable Chemistry (CSC), Chile

Abstract

Alkylamines and arylamines, which have been extensively used in many industrial processes, have been found as dangerous residues in air, soil, surface water and groundwater at risk concentrations. Therefore, they represent a prominent threat to human health and environment. Hence, the detection of volatile amines species is essential in terms of environmental safety. In this sense, luminescent chemical sensors based on Metal-Organic Frameworks (MOFs) have become a promising alternative for the sensing and monitoring of amines *in situ*.

In this study, we investigated the Turn-off luminescence mechanism of the MOF labelled UiO-67-dmbpy, which belongs to a family of robust MOFs based on octahedral [$Zr_6O_4(OH)_4$dmbpy$)_{12}$]; dmbpy: N,N'-dimethyl-2,2'-bipyridinium, reported by En-Qing *et al.* in 2017 as a selective chemical sensor to alkylamines. A theoretical study by means of the DFT (Density Functional Theory) and the TD-DFT (Time-dependent DFT) was performed. Because of a big size of the MOF, a fragmentation scheme was applied with the purpose of optimizing time and computational resources. Thus, the structure was reduced from a secondary building unit (SBU) [$Zr_6O_4(OH)_4(dmbpy)_{12}$], to a geometry containing eleven organic linkers truncated to capping formate groups [$Zr_6O_4(OH)_4(HCOO)_{11}$(dmbpy)]. Besides, an analysis of the host (MOF)–guest(alkylamines) interactions via the Morokuma-Ziegler energy decomposition scheme and the NOCV (Natural Orbitals for Chemical Valence) were carried out. The structural model proposed in this work successfully reproduces the luminescent properties of the system. Results indicate that the emission at 405 nm is linkers-centered (experimental value 411 nm). This band was assigned to the ligand centered (π-π*) transition.

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