

# Tuning the optical properties of a photocatalytic metal-organic framework by means of molecular modelling

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## Abstract

A theoretical study of reported isostructural metal-organic frameworks (MOFs) based on MIL-125-Ti<sup>4+</sup> was performed to understand the optical properties and facilitate the rational design of new materials with potentially improved features as photocatalysts. The experimentally tested MOFs (MIL-125-Ti<sup>4+</sup> labeled as M) were functionalized with -NH<sub>2</sub>, -CH<sub>3</sub>, and -OH substituents on the 1,4-benzenedicarboxylate (BDC) linker (labeled as M-NH<sub>2</sub>, M-CH<sub>3</sub>, and M-OH, respectively), generating a broadened light-harvesting of the MOF and an improvement of the N<sub>2</sub> conversion rate. The M-NH<sub>2</sub> showed the highest visible light absorption and N<sub>2</sub> photocatalysis efficiency experimentally. This substituent effect was theoretically studied via Density Functional Theory (DFT) calculations on the ground singlet (S<sub>0</sub>) and first excited state (singlet and triplet) using Time-Dependent Density Functional Theory (TD-DFT), the Morokuma-Ziegler energy decomposition scheme, and Natural Orbital of Chemical Valence (NOCV) analysis. These tools allowed for the reproduction of the optical properties and performance in good agreement with the experiment and highlight that the N<sub>2</sub> conversion rate increases as the donor character of the R group improve. This effect is a result of the stabilization of the Occupied Molecular Orbitals (localized on the BDC linker), a decrease in the charge recombination, and by an increase of charge flow to the metal center favoring the photocatalytic Ti<sup>4+</sup>/Ti<sup>3+</sup> reduction (via ligand to metal charge transfer (LMCT) transition). These systems also display a metal-ligand charge transfer (MLCT) process in the excited state favoring the emission localized in the BDC linker, which was confirmed via Complete Active Space Self-Consistent Field (CASSCF) calculation. Finally, through CASSCF, it was possible to propose two new isorecticular structures, with the -SH and -NO<sub>2</sub> substituents (labeled as M-SH and M-NO<sub>2</sub>), with the -SH variant exhibiting optical and photocatalytic properties that could rival M with -NH<sub>2</sub> substitution. © 2023 The Royal Society of Chemistry.