Tuning the Optical Properties of a Chromophore in a Nanoconfined Environment

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Abstract :

Organometallic complexes based on Ru(II)-polypyridine systems display electronic properties that are very sensitive to the local environment. A photoinduced charge transfer leads to reorganization dynamics that depend on the interactions with the solvent. We have shown that the transient electronic spectra reveal different mechanisms depending on the nature of the latter [1]. To this end, we developed a computational strategy that is based on an integrated multilevel approach providing an ad hoc intramolecular force field for the Ru complex ground and excited states to be used in classical molecular dynamics simulations. Such simulations are coupled with TD-DFT calculations of the optical properties of the chromophore in its local environment.

Nanoconfinement can lead to significant modifications of the dynamical, optical, and physicochemical properties of confined species, which can be exploited for a wide range of applications [2]. Layered double hydroxides (LDHs) are a class of claylike layered systems, the structure of which comprises positively charged mixed-metal hydroxides on the inorganic surface, with charge-compensating anions immersed in an aqueous environment, in the expandable interlayer space [3]. Some experimental work on ruthenium/LDH hybrids have shown that intercalating Ru complexes in LDHs leads to a significant improvement of their thermal and photo-stability [4]. However, a molecular interpretation of the role played by the confined environment, which is key to fine tuning the effect on intercalated compounds, is still missing.

We adapted and applied our computational approach to develop an ad hoc intramolecular force field for the Ru complex ground and excited states and model its interaction with the LDH. The influence of nanoconfinement on the absorption and fluorescence spectra of the chromophore will be discussed. In particular, we shall focus on the Ru complex – surface interactions and on the role of the surrounding water molecules. The effect of the specific confined environment of the LDH on water will be also analyzed.

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