Computational Models for Fluorescence Study on Presence of Metallic Nanoparticles

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INTRODUCTION

The optical properties of chromophores can be changed by the presence of metallic surfaces or metallic nanoparticles. It was shown to be possible to switch between quenching or enhancement of fluorescence brightness varying factors such as metal-chromophore distance, shape and size of the nanoparticle, among others.[1,2] These phenomena could be used to develop new characterization techniques, however, there is no systematic study presented in literature.

METHODS

The electronic properties of four fluorophores (the PAH's pyrene, anthracene, diphenylantracene and naphthalene) were studied using DFT and the TDDFT. To evaluate the effects of the presence of platinum nanoparticles in the emission spectrum of these compounds, we have employed a new type cluster based on the study of Piotrowski and Piquini[3] (Figure 1). TDDFT calculations (B3LYP / 6-311G) were performed to optimize and obtain the energy of the first excited state of molecules studied in the gas phase and in aqueous solution (IEFPCM).

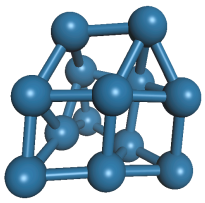

Fig. 1: Model of Piotrowski and Piquini[3] for the Pt minimum cluster.

RESULTS AND DISCUSSION

Table 1 shows that emission wavelength (λ_{max}) values obtained for the isolated PAH's with TDDFT calculations are in good agreement with experimental values. The inclusion of the solvent effect causes small bathochromic effect.

Experimental results[4] indicate that the presence of Pt cubic nanoparticles (with edge about 2Å) induces quenching of the fluorescence spectrum. These results also show that the quenching is only observed if fluorophore and nanoparticle interacts. From our calculations, there is interaction between the PAH and the metallic cluster until the distance of 8Å (Fig. 2).

Table 1: Emission wavelengths obtained with B3LYP/6-311G(d) and experimental values

	λ_{max} (nm) gas-phase	λ_{max} (nm) water	λ_{max} (nm) exp.
Pyrene	368	377	373
Anthracene	446	451	420
Diphenylanthracene	481	489	410
Naphthalene	326	329	338

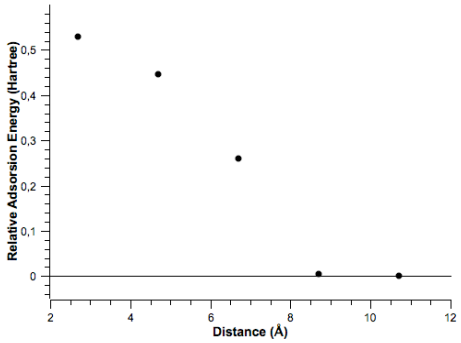

Fig. 2: Interaction energy dependence with the separation between pyrene and Pt cluster.

CONCLUSIONS

The methodology chosen for obtaining the wavelength of emission of isolated PAH's proved to be efficient. The use of Piotrowski and Piquini[3] model allows to study the interaction between fluorophore and Pt-cluster, with reduced computational costs, but getting the excited state and the electronic transition to the ground state of the fluorophores in the presence of this cluster is still a problem to be overcome.

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