Evaluation of the Photophysics of Four Ru(II) Phthalocyanine/TiO_2 (Anatase) Complexes Using DFT Methods

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Introduction

Electron transfer is the most basic form of a chemical reaction: the electron is spontaneously transferred from a donor to an acceptor center[1, 2]. The understanding of the photophysics related to the photoinduced electron transfer is fundamental for the comprehension of certain natural processes, such as light harvesting, making feasible the developing of artificial systems for solar fuel production[3].

In the study of photocatalytic processes, computational quantum mechanics has made significant contributions[4-7]. Jono and coworkers, for example, demonstrated the occurrence of interfacial charge transfer from an organic compound to the surface of titanium dioxide, using visible radiation[8].

Among the possible applications of such phenomenon stands out the use of solar energy in visible region to trigger photocatalytic processes (solar energy conversion, environmental remediation and photocatalytic production of hydrogen are some examples) since that a large part of the known semiconductor oxides with photocatalytic activity are active only in the ultraviolet. Thus, this has attracted the attention of several researchers around the world[9-20].

Considered as the energy source of the future the hydrogen, in addition of being a renewable font, concentrates a large amount of energy per unit mass (1.0 kilogram of hydrogen contains about the same energy supplied by 2.7 kilograms of gasoline), enabling the portability of energy[21,22]. Experts have pointed out three major obstacles to the expansion of hydrogen consumption, taking into account the currently available technology: clean production, low cost and the storage and transportation. As a result, many efforts to expand the use of hydrogen as cheap energy supply has been based on the development of efficient processes free of fossil fuels[16,19,20].

The photocatalytic degradation of water to produce hydrogen under the solar irradiation is a promising way to obtain clean and cheap hydrogen. Despite the advances in photocatalysis using ultraviolet radiation, the use of visible radiation is yet a theme of intense studies[16,20].

Studies show that the incorporation of photosensitizing dyes to the surface of a photocatalyst is a viable option to increment the H2 production[23-24]. TiO_2 is the most studied photocatalyst since it is stable, usually presents photocatalytic activity, of low-cost and versatile. However, this semiconductor has a negligible photocatalytic activity in almost all the visible spectrum. So, much effort has been directed to work around this problem[16,20]. One of the alternatives found are the dye-sensitized photocatalysts[16,25]. These systems are capable to minimize the recombination of the charge carriers and the red shift of the absorption spectrum enabling the use of visible radiation[16].

In the present study, we evaluate the role of functional groups on the photoinduced charge transfer in four complexes based on the chemical association between Ru(II) phthalocyanines and a cluster of anatase (TiO_2), continuing the study started by Gomes et al. (2015)[26].

Methods

To optimize the structure of the complexes 1-diethyl-1-carboxyl-RuPc-Anatase (1), 2-diethyl-1-carboxyl-RuPc-Anatase (2), 2-diethyl-2-carboxyl-RuPc-Anatase (3), and 3 -diethyl -1- carboxyl – RuPc-Anatase (4), and calculate their vibrational frequencies, we used the hybrid functional B3LYP and the basis set LANL2DZ ECP [27-29] with the corresponding pseudo- potential for Ru and Ti, and the basis set def2-TZVP[30] for the other elements. The functional CAM-B3LYP[31] was used in the TDDFT approaches for predicting the first sixty singlet excited states for the construction of the electronic spectrum of each studied derivative.

The nanocluster of anatase used in the calculation was based in a structure described by Jono and co-workers[8], being kept frozen in all calculations.

All calculations were done considering the derivatives solvated in acetonitrile. This was done using CPCM (Polarizable Conductor Calculation Model)[32].

The contribution of the molecular orbitals on electronic state was calculated using Chemissian[33]. GaussSum[34] was used to calculate the contribution of the most important electronic transitions and to build energy diagrams and graphs of states densities.

Structural optimizations, infrared frequency calculations and simulations of excited states were done using the software Gaussian 09[35].

Results and Discussion

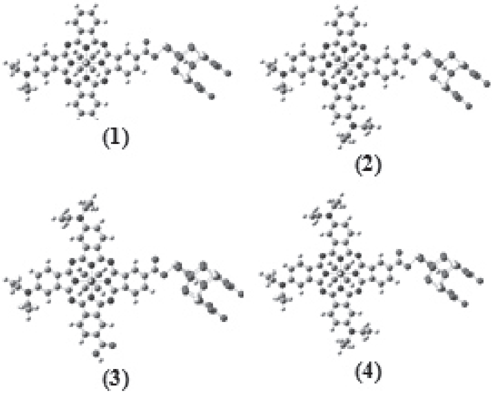

Figure 1. Optimized structures: (1) 1-diethyl-1- carboxyl-RuPc-Anatase (2) 2-diethyl-1-carboxy- RuPc-Anatase (3) 2-diethyl-2-carboxyl-FtRu-Anatase (4) 3 -diethyl -1- carboxyl – RuPc- Anatase

The vibrational spectra calculated for the derivatives did not have imaginary frequencies, indicating that the stationary point found on the optimization corresponds to global minima.

The values of the geometric parameters of each structure show good agreement with typical bonds and angles observed of similar structures[36-38].

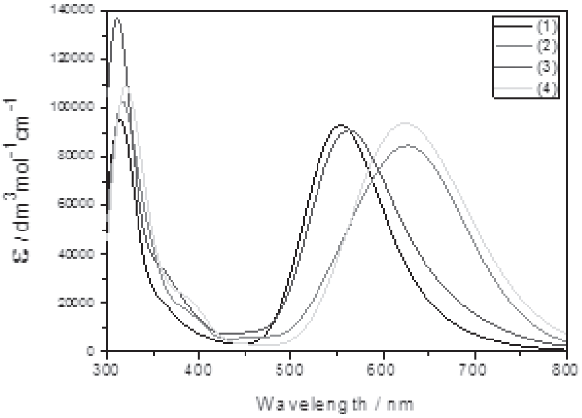

Figure 2. Simulated electronic absorption spectra of the complexes (1) to (4) solvated in acetonitrile.

The simulated spectra of these complexes exhibit the two characteristic absorption bands typical of phthalocyanines[39]. This suggests that the light absorption properties observed for the ruthenium phthalocyanines under study are preserved in these complexes. The maintenance of these properties may represent a significant advantage for use of these complexes in applications based on sunlight absorption[40-43].

The shifts observed in the Q-bands suggest that the nature, position, number of substituents in the macrocycle, and chemical bonding with TiO2 exert great influence on the electronic structure of the complexes. The complexes (2) and (4) that have a greater number of donor substituents present a red-shifted Q-band.

Complexes (2) and (4) have both absorption bands red shifted relative to the others. These complexes present in general expressive values of oscillator strength for the first five excited states, typical of electronic transitions of high probability. They are related to photoinduced charge transfer from donor groups, and are in the range of the Q-band. Differently, for complexes (1) and (3) the most intense electronic transitions are related to states S4 and S5. Different combinations and weights of the molecular orbitals in the range between HOMO-2 and LUMO+3, excluding the LUMO, are involved in the transitions that constitute the five first electronic states of these four complexes.

The Soret (B) band in these complexes is of high probability, involves high electronic states and practically does not suffer electronic shift. However, the intensity of the bands varies, being the most intense related to complex (3). This complex possesses donor and acceptor groups linked to the macrocycle. The analysis of the orbital structure of this band suggests that it is mainly of charge transfer from the macrocycle and metallic center of phthalocyanine to the semiconductor.

Table 1 presents the contribution of main molecular fragments (Ru(II), the TiO_2 cluster - TiO_2, the free base phthalocyanine - Mcycle, the donor groups - Donor, and the axial pyridines - Py) in the molecular orbital composition of each complex.

The data from Table 1 shows that the TiO_2 cluster does not contributes with the occupied orbitals. However, this contribution is very significant in the virtual orbitals, according to the verified in the analysis of the molecular orbitals involved in photoinduced charge transfer.

Ru(II), as well as, the free base phthalocyanine type structure and the donor groups have expressive contribution in the occupied orbitals, mainly HOMO-2 and HOMO-1 in all complexes, and HOMO-4 in the complex (4). Such orbitals are important in the Q-band, as observed in the electronic spectra (Figure 2), and in the electronic delocalization in these phthalocyanines.

The analysis of the DOS (Figure 3) corroborates with the

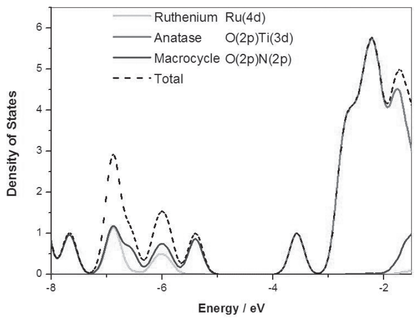

Figure 3. Density of states (DOS) diagram calculated for the complex (4), presenting the partial DOS corresponding to Ru(II), macrocycle and anatase.

Table 1. Contributions of molecular orbitals in the main areas of each complex

	MO	Contribution (%)				
		Ru(II)	TiO2	Mcycle	Donor	Py
1	H-5	-	-	98	-	2
	H-2	54	-	41	-	5
	H-1	24	-	70	3	3
	H	10	-	71	18	1
	L+1	-	99	1	-	-
	L+3	-	100	-	-	-
	L+23	8	6	83	-	3
	L+28	-	100	-	-	-
2	H-7	1	-	97	1	1
	H-6	1	-	96	1	2
	H-2	35	-	56	7	2
	H-1	31	-	48	19	2
	H	3	-	85	-	12
	L+1	-	100	-	-	-
	L+3	-	99	1	-	-
	L+23	-	99	1	-	-
	L+24	-	95	5	-	-
3	H-6	-	-	96	4	-
	H-2	34	-	56	7	3
	H-1	30	-	48	19	3
	H	4	-	85	11	-
	L+1	-	100	-	-	-
	L+2	-	100	-	-	-
4	H-7	12	-	82	1	5
	H-4	49	-	51	-	-
	H-2	26	-	51	20	3
	H-1	23	-	50	25	2
	H	2	-	82	16	-
	L+1	-	100	-	-	-
	L+2	-	100	-	-	-
	L+3	-	98	2	-	-
	L+13	-	99	1	-	-
	L+14	-	100	-	-	-
	L+23	-	99	1	-	-
	L+25	-	100	-	-	-

data of Table 1. The partial DOS of anatase predominates above – 4 eV, in the range of virtual states, showing that the electronic transitions governed by the Q-band tend to induce electron transfer from phthalocyanine to 3d states of the fivefold coordinated titanium atoms44. Additionally, the involvement of 4d orbitals of Ru(II) in these transitions is evidenced by two bands in the DOS diagrams calculated for these complexes.

Conclusions

The photophysical characterization of four complexes formed by chemical association between derivatives of Ru(II) phthalocyanine and anatase nanocluster showed, through electronic structure analysis, that the electronic excitation of the Q-band of such complexes results in the efficient electron transfer from phthalocyanine to TiO_2 (anatase). Also, the number of donor groups, peripheral to the macrocycle, favors this process and is responsible for a red shift of the Q-band, and that this band should occur in the visible, above 500 nm. This opens the possibility of applications of such complexes to enhance photocatalytic processes by sensitization of photosensitizers based on TiO_2 using sunlight.

The DOS diagram shows that the most effective contributions in the sensitization process are due to the macrocycle and Ru(II).

Acknowledgments

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