

Review Article

Physical Insights into Molecular Sensors, Molecular Logic Gates, and Photosensitizers in Photodynamic Therapy

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In this article, the importance of charge/electron transfer in two rapidly growing areas of science is highlighted. In the field of molecular sensors, it plays a considerable role on the detection of molecular systems to serve as fluorescence sensors, switches, and molecular logic gates (MLG) replacing the semiconductor electronics, while in the field of photodynamic therapy, it acts competitive. On these scientific fields, a lot of research has been conducted in the last decades to find out potential candidates. In the field of fluorescent sensors, switches, and molecular logic gates, the fluorescent photo-induced electron transfer switching principle is responsible for the quenching of fluorescence. The manipulation of the quenching can lead to the design of an ideal candidate for complicated molecular logic operation. In the field of photodynamic therapy (PDT), the intersystem crossings occurring between excited singlet and triplet states are the key for an ideal photosensitizer (PS) candidate. The triplets must present relatively long lifetimes, and they must lie near or above the energy which is needed for the excitation of molecular oxygen. In this case, charge/electron phenomena can act competitive, and they are not desirable. However, there are a few complexes which are good PSs of singlet oxygen despite the charge transfer (CT) nature of their lowest excited state.

1. Introduction

In the last forty years, a great deal of research has been devoted to the study of the intramolecular electron or charge transfer and energy transfer phenomena [1–28] because they play a fundamental role in many areas of chemistry and biology, i.e., in chemical reactions [1, 2, 18], in photocatalysis, [20] in biochemical and biological processes [29], in chemical sensors and fluorescent probes [8, 9, 30, 31], in the design of optoelectronic devices [32], in energy conversion [23, 24, 28, 31, 33], in quantum dots [19, 25], and in material science [20, 28, 34].

There are four theories, which each one separately, but also all together help in deeply understanding of the study of the charge transfer (CT) phenomenon. There are (a) the theory of “charge transfer” of R. S. Mulliken (Nobel laureate 1966 in Chemistry) [35, 36], (b) The theory of mechanisms of “outer/inner sphere” of H. Taube [37, 38], (c) the theory of

“two state non-adiabatic” of Marcus [39, 40] and (d) the “intervalence” theory of Hush [41, 42]. For a detailed review on the four theories, refer [10] and reference therein. The theory of Marcus [39, 40] is the most commonly used theory, and it is based on a model of coupling between the electronic potential energy surfaces of donor and acceptor states. This model requires detailed knowledge of the potential energy surfaces of the electronic states of the donor and of the acceptor moieties, and this is impossible to be achieved for polyatomic systems. Simplified schematic diagrams of the variation of energy are drawn along a generalized reaction coordinate which usually corresponds to the most critical nuclear motion accompanying the electron transfer process [17].

What follows the photo-induced electron transfer (PET) is explained (Section 1), its important role to the detection of molecular systems to serve as fluorescence sensors, switches, and molecular logic gates replacing the

semiconductor electronics is analyzed (Section 2), while its competitive role in photodynamic therapy (PDT) is reported (Section 3). Additionally, physical insights into mechanisms occurring in molecular sensors, molecular logic gates, and photosensitizers in photodynamic therapy are reported.

2. Photo-Induced Electron Transfer

Photo-induced electron transfer, [17, 43] or PET, is the phenomenon observed in a system that has an electron donor (D) and an electron acceptor (A) part. In some systems, more than one donor or acceptor groups exist [5]. The entire system is in its ground state. Then, the donor or the acceptor part can become excited. (a) In some cases, the donor moiety absorbs radiation and it becomes excited ($D \rightarrow D^*$). Thereafter, the system is converted fully or partially to a charge transfer state (CT) where an electron or a part of electron charge is transferred from D^* to A ($D^* \rightarrow D^+ - A^-$) (Figure 1(a)). This phenomenon is observed in photovoltaics. (b) In the case of fluorescent sensors, the acceptor part absorbs light and results in being excited ($A \rightarrow A^*$). Then, the emission of A^* is *suppressed* by the PET phenomenon from D to A (Figure 1(b)).

The PET process is notably useful, as the signal depends on special circumstances such as structural and energetic factors. It is either an “on-off” or “off-on” type [43], resulting in a well-defined “digital” response. PET yields very sharp changes in the signal intensity, while it keeps the emission wavelength unchanged [44]. On the contrary, internal charge transfer (ICT) [45, 46] can be adjusted in such a way to generate changes in the absorption or emission wavelengths. Thus, PET and ICT phenomena could play a useful role on the prediction of fluorescence sensors, switches, and molecular logic gates replacing the semiconductor electronics.

An example of a fluorescent sensor is presented here where the number of spacers between donor and acceptor moiety influences its emission spectrum. The sensor is a tertiary amine-pyrene molecule (inset of Figure 2), and it acts as a sensor of organophosphorus nerve agent mimics. Quenching of pyrene emission has been observed both experimentally and theoretically in these systems to a different extent depending on the number of spacer units, due to photo-induced electron transfer from the *t*-amine to pyrene [8, 9, 17]. The probability for charge transfer is decreased with increasing number of CH_2 spacer units between the *t*-amine and the pyrene; for instance, the excitation probability of the CT state is larger by an order of magnitude in the system with one CH_2 unit compared to the system with four CH_2 units [17]. Moreover, as the number of spacer CH_2 units between *t*-amine and pyrene increases, the barrier (BE, Figure 2) between the minimum of the S_1 state and the avoided crossing also increases, and as a result, the emission is retained. Finally, the *f*-values of the wavelengths of the CT states for the case of the system having only one CH_2 unit is small, which is expected because it is a CT state, but it is not zero, while for the system having four CH_2 units, it is zero (Table 1).

3. Sensors, Switches, and Molecular Logic Gates

A molecular logic gate is a molecule that performs a logical operation using one or more logic inputs and produces a single logic output. The ability of molecules for processing information similar to electronic systems was first demonstrated by de Silva et al. [47] in 1993, and eventually, this idea opened up a rapidly growing multidisciplinary research area which provides a novel mental platform to build new ideas [48–54]. Molecules can be subject to changes in their ground or excited states, in response to modulators which can be other molecules, cations, anions, or light of a certain wavelength, solution pH, and solvent polarity [14, 48–54]. In most cases, these changes could then be observed by changes in the absorption or emission intensity, or wavelength, and can be related to the operation of logic gates, via the familiar Boolean logic [44]. The modulators correspond to the inputs, and the observed changes correspond to the outputs. It is both very interesting and important that molecular logic gate design may not be subject to the same limitations as the silicon-based analogues. Phenomena such as superposed logic sometimes referred to as wavelength-reconfigurable logic are unavailable to semiconductor electronics. They are available only to molecular logic gates which are more versatile than their silicon counterparts [44, 51]. In addition, a single molecule can be designed to simultaneously behave as two (or more) distinct logic gates, depending on the exact choice or definition of outputs [44, 51, 54–59].

In the case of the intermolecular PET process, there is an intramolecular “fluorophore-spacer-receptor” system. The fluorophore is the fragment that is capable of serving as an “antenna” for the absorption of photons resulting in a transformation of its molecular structure, and the receptor is the fragment whose reactivity alters as a result of the structural transformation. This principal is applied in natural photosensitive systems [51]. There are two different molecular structures of a system. In the first one, the receptor is free of the target species, and in the second one, the receptor binds the target. When the fluorescence emission is switched off in the first structure due to a PET process and switched on in the second one that system is a fluorescent PET sensor that corresponds to a simple YES molecular logic gate. If the fluorescence emission is switched on in the first structure and it is quenched in the second one, that system is a sensor that corresponds to a NOT molecular logic gate. If the system consists of more than one receptor units and/or more modulators are changed, then the system has the potential for more additional molecular logic gates operations, such as NOR, XOR, XNOR, INHIBIT, and IMPLICATION [14, 48–51].

Molecular fluorescence sensors and switches correspond to YES or NOT molecular logic gates. Thus, the field of molecular fluorescence sensors and switches is a simplified version of molecular logic gates, and it is more studied than the general field of molecular logical gate, which presents increasing complexity [51]. Its real applications using working models are limited up to now; however, there are some applications achieving commercial success such as specific sensors for sodium, potassium, and calcium which are used as

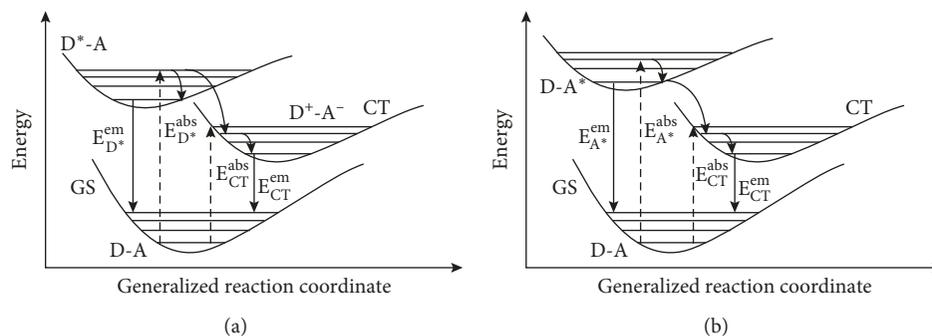
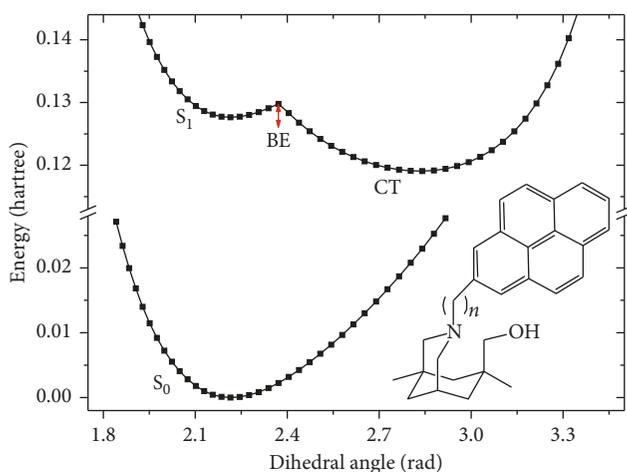


FIGURE 1: Photo-induced electron transfer for cases (a) and (b).

FIGURE 2: Potential energy curves of the ground (S₀), the first excited state (S₁), and CT state of the *t*-amine-pyrene molecule with 4 CH₂ spacers with respect to the dihedral angle of the N atom of the amine at the B3LYP/6-31G(d,p) level of theory. Inset: *t*-Amine-pyrene molecule, with *n* numbers of CH₂ spacer units.TABLE 1: Absorption, emission, and CT transition λ (nm) and f -values of tertiary amine-pyrene molecules at the B3LYP and PBE0/6-31G(d,p) levels of theory.

Spacer	Method	Absorption (S ₀ → S ₁)		Emission (S ₁ → S ₀)		CT → S ₀	
		λ	f	λ	f	λ	f
-CH ₂ -	B3LYP ^a	342.8	0.347	373.1	0.413	525.4	0.002
	PBE0	333.5	0.376	363.9	0.446	550.5	0.006
	Expt ^b	342					
-(CH ₂) ₄ -	B3LYP ^a	342.8	0.338	372.1	0.401	495.5	0.000
	PBE0	333.4	0.362	362.9	0.428	453.1	0.000

^aReference [17]. ^bReference [8]. Experimental data are also given.

the platform of a portable diagnostic tool, i.e., a blood gas analyzer for hospital critical care units and ambulances [52]. Thus, many groups both experimental and theoretical are working intensively in the topic of molecular fluorescence sensors, switches, and logic gates. Chemists, molecular biologists, engineers, and other scientists, separately or in collaboration, focus on enzymes, dyes, and small molecules to find out appropriate molecular systems to serve as simple or more complicated molecular logic gates [47–60].

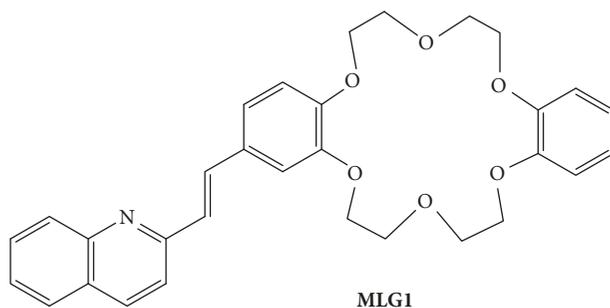
Two examples of molecular logic gates are given. In the first example, the molecule can behave as a multiple distinct logic gate, depending on the choice of the outputs. Namely, the benzo-18-crown-6-ether of the styrylquinoline molecule (**MLG1**, Scheme 1), in acetonitrile solvent, acts as a sensor for Ca²⁺ cation and as a molecular logical gate using H⁺ and Ca²⁺ and irradiation as inputs. Our calculations have shown that there are 8 thermally stable forms, i.e., *trans* and *cis* isomers of neutral, N-protonated, complexed with Ca²⁺, and both N-protonated and Ca²⁺ complexed, with different absorption and emission spectra. These forms can be interconverted from one to another. The emission output at 500, 470, 430, and 407 nm can be utilized as output to build AND, NOR, XOR, XNOR, INHIBIT, and IMPLICATION logic gate [14]. The corresponding truth table is presented in Table 2, and the molecular logic operations are given in Table 3. Analytically, the conditions are presented in [14].

A second example of the MLG system presented here is a styryl-bodipy derivative (**MLG2**), which acts as a three metal-cation-receptor fluorophore (Scheme 2). The emission of the single fluorophore, of the monometallic, and of the dimetallic complexes is quenched, while the emission of the trimetallic complex of fluorophore is retained. [44] As a result, the **MLG2** can act as a three input AND MLG. Our new theoretical data presented here are calculated at the B3LYP/6-31G(d,p)LANL2TZ_{Hg} level of theory, and they are in very good agreement with the experimental data (Table 4).

4. Photodynamic Therapy

The successful use of light in the treatment of diseases has been known for many centuries. Photodynamic therapy (PDT) is a treatment involving light and a chemical substance which is called photosensitizer (PS). PS in conjunction with the molecular oxygen leads to cell death. In more details, PDT is a selective treatment modality for the local destruction of diseased cells and tissue. The selectivity is based on the ability of the PS to preferentially accumulate in the diseased tissue and efficiently generate singlet oxygen or other highly reactive oxygen species (ROS) such as radicals, which induce the target cell death. [61, 62].

The ground state of oxygen is a triple state X³Σ_g⁻. The first excited a¹Δ_g and the second excited state b¹Σ_g⁺ are lying 0.98 and 1.63 eV above the ground state [63] (Figure 3). The b¹Σ_g⁺ state is very short lived and relaxes quickly to the lowest lying



SCHEME 1

TABLE 2: Truth tables resulting from **MLG1** using irradiation, H^+ , and Ca^{2+} inputs and the emission mode as output.^a

Input 1: (irradiation) ^b	Input 2: H^+	Input 3: Ca^{2+}	Output 1: 500 nm	Output 2: 470 nm	Output 3: 430 nm	Output 4: 407 nm
0	0	0	0	0	1	0
1	0	0	1	0	0	0
0	1	0	0	1	0	0
1	1	0	1	0	0	0
0	0	1	0	0	0	1
1	0	1	0	0	1	0
0	1	1	0	0	1	0
1	1	1	1	0	0	0

^aReference [14]; M06-2X and PBE0/6-31G(d,p) level of theory. ^bIrradiation by light at 770 nm results in enrichment of the *cis* isomer of **MLG1** and 939 nm results in enrichment of the *trans* isomer.

TABLE 3: Molecular logic operation for **MLG1** starting from **MLG1** enriched in the *trans* isomer using two ionic inputs and photoisomerization input and emission mode in nm.^a

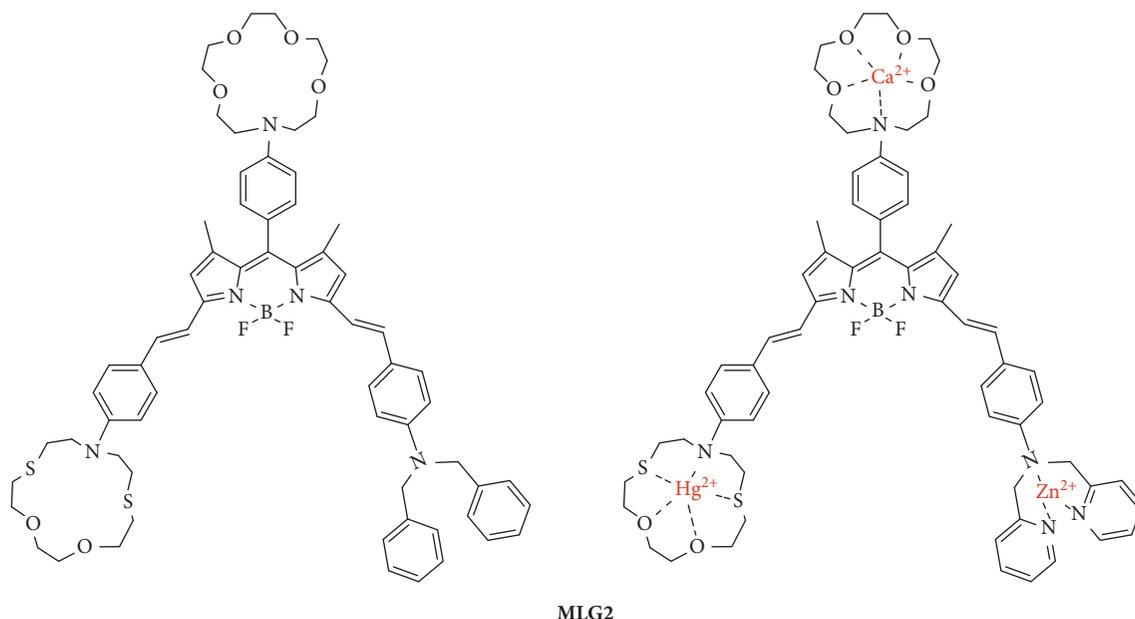
Irradiation ^b + H^+ (without Ca^{2+})	INHIBIT ^c (470 nm); NOR (430 nm)
Irradiation ^b + H^+ (with Ca^{2+})	AND (500 nm); XOR (430 nm); NOR (407 nm)
H^+ + Ca^{++} (no irradiation ^b)	INHIBIT ^c (470 nm); XNOR (430 nm); INHIBIT ^d (407 nm)
H^+ + Ca^{++} (after irradiation ^b)	IMPLICATION ^e (500 nm); INHIBIT ^d (430 nm)
Irradiation ^b + Ca^{++} (without H^+)	INHIBIT ^f (500 nm); XNOR (430 nm); INHIBIT ^d (407 nm)
Irradiation ^b + Ca^{++} (with H^+)	NOR (470 nm); INHIBIT ^d (430 nm)

^aReference [14]; M06-2X and PBE0/6-31G(d,p) level of theory. ^bDepending on the initial structure for the **MLG1**, i.e., 770 (for *trans*), 734 (*trans-H⁺*), and 685 nm (*trans-Ca⁺⁺*). ^cThe first input is H^+ . ^dThe first input is Ca^{++} . ^eThe first input is Ca^{++} . ^fThe first input is the irradiation.

$^1\Delta_g$ excited state. [63] The first excited state is known as singlet oxygen (1O_2), and it has been implicated in many redox processes in biological systems. For many years, it has been characterized as a deleterious chemical species, even though many positive clinical applications in the PDT of cancer have been presented. Recently, many ROS, including 1O_2 , attract considerable researcher's attention because of their role in physiological signaling, like cell proliferation or tissue regeneration [64]. The excited 1O_2 can undergo deactivation through different pathways: nonreactive (phosphorescence, internal conversion, and physical quenching) and reactive (electron transfer, peroxide, and endoperoxide). Thus, it can present a radiative transition to the ground state, emitting a phosphorescent photon at 1270 nm or 1590 nm. Moreover, it can transform the electronic excitation energy directly to vibration and, eventually, heat. This can happen without external influence (internal conversion) or through interactions with other compounds (physical quenching), like a solvent (for instance water). Furthermore, 1O_2 can engage in chemical reactions, i.e., in endoperoxide

formation, in peroxide formation, and in electron transfer reactions. It is feasible to directly excite ground state oxygen 3O_2 to 1O_2 through absorption of light energy or photons of certain energy. Totally, there are two types of transitions: monomol (M) and dimol (D). In monomol transitions, one photon is absorbed by a single 3O_2 molecule, and thus the molecule becomes excited electronically. In dimol transitions, one photon ($h\nu$) is absorbed by a momentary complex formed by two ground state 3O_2 molecules; and both molecules become excited. It should be noted that dimol bands are relatively weak in comparison to the monomol transitions, and this is an important argument discouraging their use in redox biology in favor of monomol excitations.

The mechanism of PDT is based on the characteristics of the PS substance. Initially, PS is lying in its ground state (S_0) (Figure 3). Then, the PS absorbs radiation, and it becomes excited in its first excited state (S_1) or in another excited state. Via internal conversion, the PS populates the S_1 state. Via an intersystem crossing, PS efficiently populates an excited triplet state T_2 or T_1 , while via internal convention



MLG2

SCHEME 2: Single fluorophore (MLG2) and the trimetallic complex of fluorophore.

TABLE 4: Absorption and emission λ_{\max} (nm) at the B3LYP level of theory in acetonitrile solvent of uncomplexed MLG2, of monometallic, and trimetallic complexes of MLG2 in acetonitrile solvent.

	Absorption	Emission
MLG2	646 (692)	—
MLG2- Ca^{2+}	700 (672)	—
MLG2- Zn^{2+}	651 (668)	—
MLG2- Hg^{2+}	666 (630)	—
MLG2- Ca^{2+} - Zn^{2+} - Hg^{2+}	623 (626)	683 (656)

^aReference [44]. ^aThe experimental values are given in parentheses.

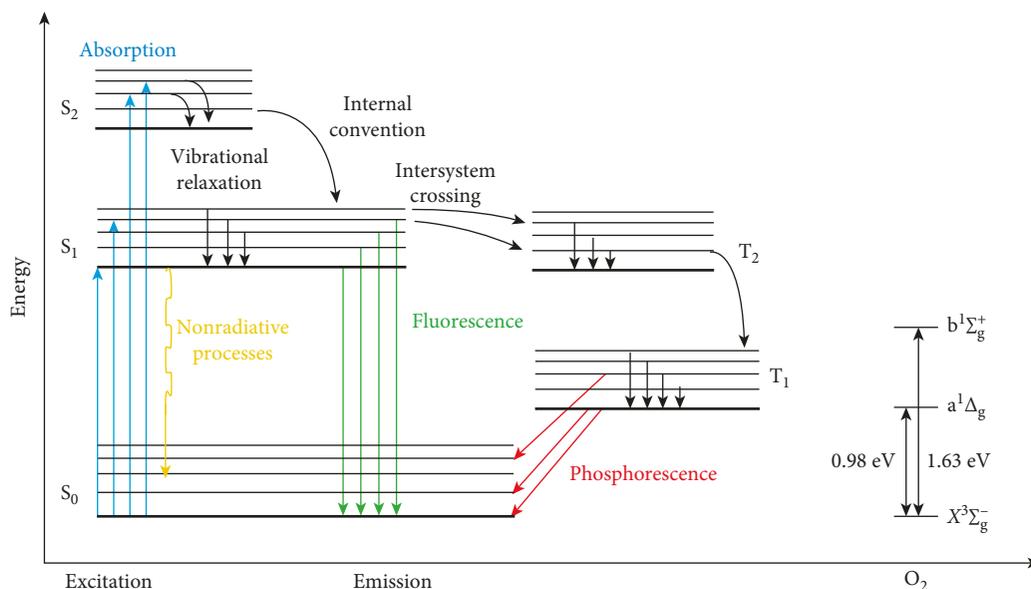


FIGURE 3: A Jablonski diagram and the electronic states of the oxygen molecule.

the population of T_1 can be increased. The PS in the triplet state can produce toxic reactive oxygen species (ROS), such as $^1\text{O}_2$ or free radicals, by two different pathways; i.e., it can

react with molecules to generate intermediate free radicals that can generate ROS (type I photochemistry) or, it can directly interact with molecular oxygen in its ground triplet

state ($^3\text{O}_2$) to produce *in situ* cytotoxic $^1\text{O}_2$ through an energy transfer process (type II photochemistry). The type II is the most relevant PDT mechanism in cells because most PSs effectively produce $^1\text{O}_2$ [65, 66]. The ROS which are generated can cause irreversible damage when it is generated inside cells, mainly inside subcellular organelles (e.g., mitochondria) where PSs is localized and accumulated [65]. Therefore, PDT would selectively kill diseased cells [67].

For a successful use of PDT, the choice of an appropriate PS is a crucial matter [61, 62, 67, 68]. The main properties of ideal PS for PDT are (1) chemical purity, (2) high quantum yield of singlet oxygen production, (3) significant absorption at the long wavelength region (600–800 nm), (4) high preferential tumour localization, (5) minimal dark toxicity and delayed phototoxicity, and (6) stability and ease to dissolve in the injectable solvents [61, 62, 67, 68]. In addition, a PS candidate must have relatively long lifetimes in the triplet state. This can be achieved mainly via (i) the incorporation of metals and mainly heavy metals which lead to an increase of the triplet state lifetime due to the increasing intersystem crossing process [65, 69, 70] and (ii) via the design of molecules capable of absorbing two photons simultaneously. Up to now, many porphyrinoid and non-porphyrinoid PSs, either hydrophobic or hydrophilic, have been studied. Some of them are very good candidates as PDT agents. The nonporphyrinoid PSs include anthracyclines, cyanines, hypericin, hypocrellins, phenothiazinium, psoralens, fullerenes, bodipy, and squarines groups [61, 65, 71–77].

In the case of the PDT, when the PS has a donor and an acceptor unit, the CT state of the PS can act competitive to the triplet states and it is not desirable. It is well-known that charge transfer can decrease the $^1\text{O}_2$ production by quenching of the excited state [78]. However, there are complexes such as Ru(II) bipyridine that are good PSs of the singlet oxygen in spite of the charge transfer (CT) nature of the lowest excited state of these compounds. This happens because of the relatively long lifetimes of the triplet metal-ligand CT states of many Ru(II) coordination compounds that make these excited states susceptible to quenching by oxygen.

5. Conclusions

In this review article, the importance of charge/electron transfer in two rapidly growing areas of science, i.e., in the field of molecular logic gates which also includes the field of molecular sensors and switches as a simplified version of the molecular logic gates and in the field of photodynamic therapy, is outlined. On both scientific fields, a lot of research has been conducted in the last decades in order to design potential candidates to act as molecular sensors and molecular logic gates and as photosensitizers for photodynamic therapy. The main points which lead to ideal candidates for these two scientific fields are summarized below.

In the field of molecular logic gates (MLG), the commonly used basic steps for the design of an ideal candidate for complicated molecular logic operation are (i) the

candidates consist of at least one donor and one acceptor unit, (ii) the fluorescent photo-induced electron transfer is desirable, and (iii) the candidates are subject to changes in their ground or excited states, in response to modulators. Thus, if these changes are observed by intense and easily measurable changes in the absorption or emission intensity, or wavelength, then they can be related to the operation of logic gates.

In the field of photodynamic therapy (PDT), an ideal photosensitizer (PS) candidate must be present: (i) intersystem crossings between its excited singlet and triplet states, (ii) triple states which lie near or above the energetic needs of the excitation of molecular oxygen, (iii) long-lived triplet excited states, (iv) high chemical purity, (v) high yield of singlet oxygen production, (vi) significant absorption at the wavelength region (600–800 nm), (vii) high preferential tumour localization, (viii) minimal dark toxicity and delayed phototoxicity, and (ix) stability and ease to dissolve in the injectable solvents. In general, good candidates are the transition metal complexes which show strong visible light absorption and long-lived triplet excited states. Finally, it should be noted that contrary to the field of MLG and sensors, in most cases in PDT, the existence of charge or electron transfer between a donor and an acceptor unit of the photosensitizer can act competitive to the population of triplet states and it can lead to a reduction of the $^1\text{O}_2$ production via the quenching of the excited state.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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