

## Review Article

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

Demeter Tzeli  and Ioannis D. Petsalakis

*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., Athens 116 35, Greece*

Correspondence should be addressed to Demeter Tzeli; [dtzeli@eie.gr](mailto:dtzeli@eie.gr)

Received 30 August 2018; Accepted 18 December 2018; Published 16 January 2019

Academic Editor: Ewa Schab-Balcerzak

Copyright © 2019 Demeter Tzeli and Ioannis D. Petsalakis. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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  $\text{CH}_2$  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  $\text{CH}_2$  unit compared to the system with four  $\text{CH}_2$  units [17]. Moreover, as the number of spacer  $\text{CH}_2$  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  $\text{CH}_2$  unit is small, which is expected because it is a CT state, but it is not zero, while for the system having four  $\text{CH}_2$  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

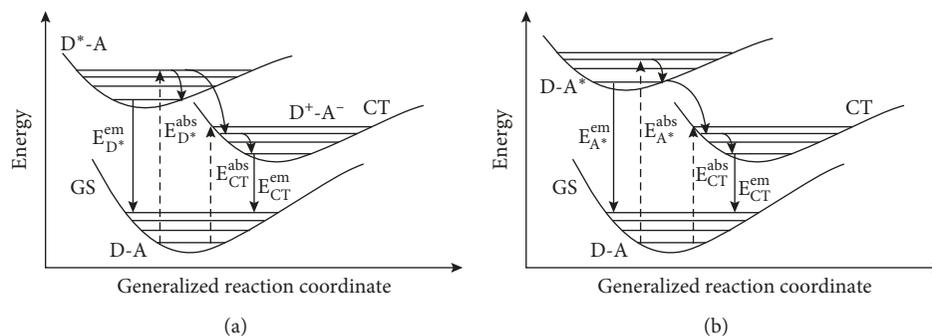
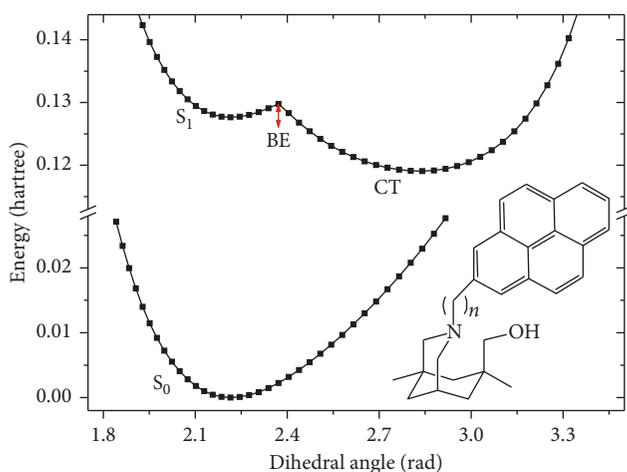


FIGURE 1: Photo-induced electron transfer for cases (a) and (b).

FIGURE 2: Potential energy curves of the ground ( $S_0$ ), the first excited state ( $S_1$ ), and CT state of the *t*-amine-pyrene molecule with 4 CH<sub>2</sub> 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 CH<sub>2</sub> spacer units.TABLE 1: Absorption, emission, and CT transition  $\lambda$  (nm) and  $f$ -values of tertiary amine-pyrene molecules at the B3LYP and PBE0/6-31G(d,p) levels of theory.

Spacer	Method	Absorption ( $S_0 \rightarrow S_1$ )		Emission ( $S_1 \rightarrow S_0$ )		CT $\rightarrow S_0$	
		$\lambda$	$f$	$\lambda$	$f$	$\lambda$	$f$
-CH <sub>2</sub> -	B3LYP <sup>a</sup>	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 <sup>b</sup>	342					
-(CH <sub>2</sub> ) <sub>4</sub> -	B3LYP <sup>a</sup>	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

<sup>a</sup>Reference [17]. <sup>b</sup>Reference [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].

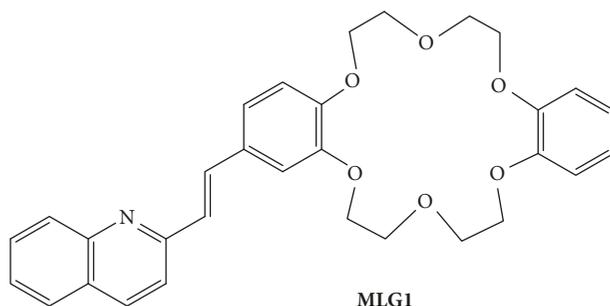
Two examples of molecular logic gates are given. In the first example, the molecule can behave as a multiple distinct logic gate, depending on the choice of the outputs. Namely, the benzo-18-crown-6-ether of the styrylquinoline molecule (**MLG1**, Scheme 1), in acetonitrile solvent, acts as a sensor for Ca<sup>2+</sup> cation and as a molecular logical gate using H<sup>+</sup> and Ca<sup>2+</sup> 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 Ca<sup>2+</sup>, and both N-protonated and Ca<sup>2+</sup> 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<sub>Hg</sub> 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  $X^3\Sigma_g^-$ . The first excited  $a^1\Delta_g$  and the second excited state  $b^1\Sigma_g^+$  are lying 0.98 and 1.63 eV above the ground state [63] (Figure 3). The  $b^1\Sigma_g^+$  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.<sup>a</sup>

Input 1: (irradiation) <sup>b</sup>	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

<sup>a</sup>Reference [14]; M06-2X and PBE0/6-31G(d,p) level of theory. <sup>b</sup>Irradiation 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.<sup>a</sup>

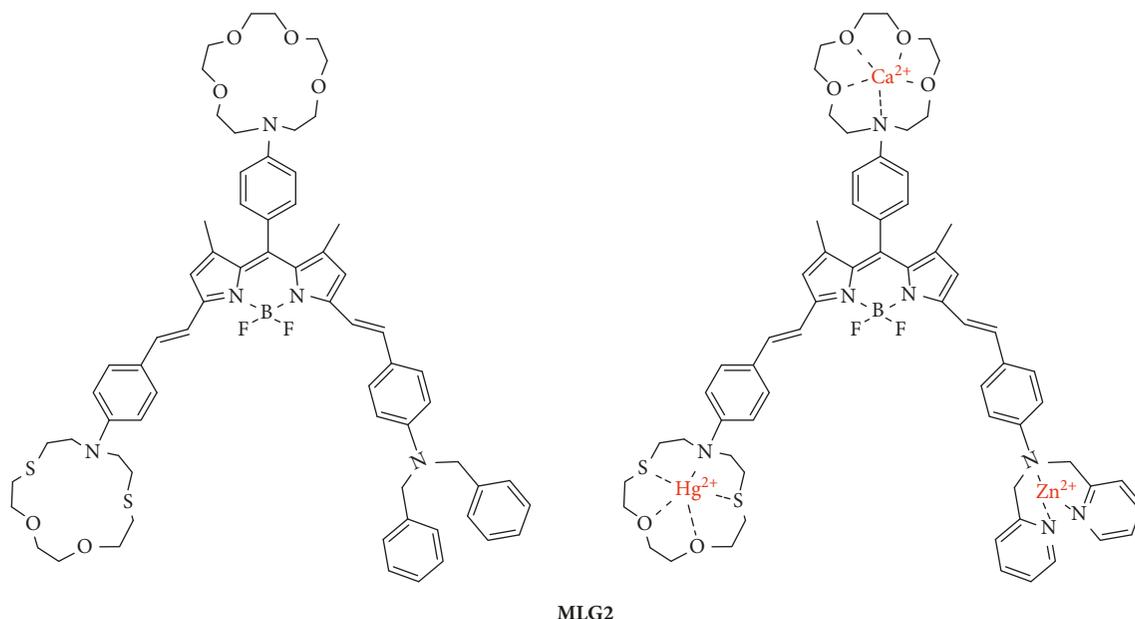
Irradiation <sup>b</sup> + $H^+$ (without $Ca^{2+}$ )	INHIBIT <sup>c</sup> (470 nm); NOR (430 nm)
Irradiation <sup>b</sup> + $H^+$ (with $Ca^{2+}$ )	AND (500 nm); XOR (430 nm); NOR (407 nm)
$H^+$ + $Ca^{++}$ (no irradiation <sup>b</sup> )	INHIBIT <sup>c</sup> (470 nm); XNOR (430 nm); INHIBIT <sup>d</sup>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

<sup>a</sup>Reference [14]; M06-2X and PBE0/6-31G(d,p) level of theory. <sup>b</sup>Depending on the initial structure for the **MLG1**, i.e., 770 (for *trans*), 734 (*trans-H<sup>+</sup>*), and 685 nm (*trans-Ca<sup>++</sup>*). <sup>c</sup>The first input is  $H^+$ . <sup>d</sup>The first input is  $Ca^{++}$ . <sup>e</sup>The first input is  $Ca^{++}$ . <sup>f</sup>The 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  $\lambda_{\max}$  (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- $\text{Ca}^{2+}$	700 (672)	—
MLG2- $\text{Zn}^{2+}$	651 (668)	—
MLG2- $\text{Hg}^{2+}$	666 (630)	—
MLG2- $\text{Ca}^{2+}$ - $\text{Zn}^{2+}$ - $\text{Hg}^{2+}$	623 (626)	683 (656)

<sup>a</sup>Reference [44]. <sup>a</sup>The experimental values are given in parentheses.

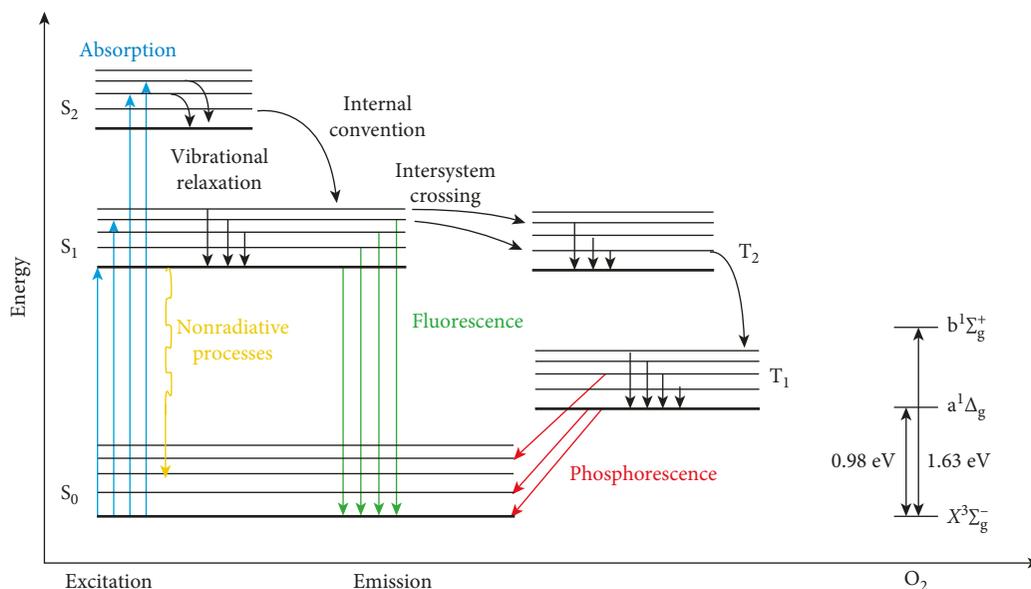


FIGURE 3: A Jablonski diagram and the electronic states of the oxygen molecule.

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 nonporphyrinoid 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

This work was supported by the project “Advanced Materials and Devices” (MIS 5002409) which was implemented under the “Action for the Strategic Development on the Research and Technological Sector,” funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014–2020) and cofinanced by Greece and the European Union (European Regional Development Fund).

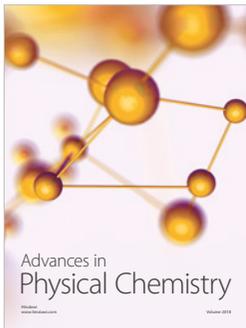
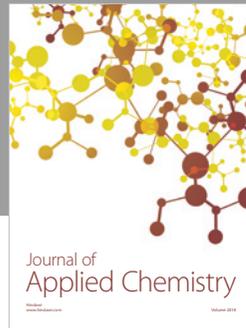
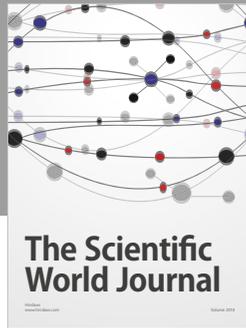
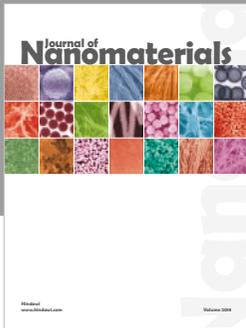
## References

- [1] A. G. Griesbeck and J. Mattay, *Synthetic Organic Photochemistry*, Marcel-Dekker, New York, NY, USA, 2005.
- [2] H. D. Roth, *Photoinduced Electron Transfer I*, Vol. 5, Springer-erlag, Heidelberg, Germany, 1990.
- [3] M. D. Newton, “Control of electron transfer kinetics: models for medium reorganization and donor-acceptor coupling,” in *Advances in Chemical Physics*, J. Jortner and M. Bixon, Eds., vol. 1, pp. 303–375, John Wiley and Sons, New York, NY, USA, 1999.
- [4] W. B. Davis, W. A. Svec, M. A. Ratner, and M. R. Wasielewski, “Molecular-wire behaviour in p-phenylenevinylene oligomers,” *Nature*, vol. 396, no. 6706, pp. 60–63, 1998.
- [5] S. Creager, C. J. Yu, C. Bamdad et al., “Electron transfer at electrodes through conjugated “molecular wire” bridges,” *Journal of the American Chemical Society*, vol. 121, no. 5, pp. 1059–1064, 1999.

- [6] I. D. Petsalakis and G. Theodorakopoulos, "Molecular orbital assistance in the design of intramolecular and photoinduced electron transfer systems," *Chemical Physics Letters*, vol. 525-526, pp. 105-109, 2012.
- [7] G. Pourtois, D. Beljonne, J. Cornil, M. A. Ratner, and J. L. Brédas, "Photoinduced electron-transfer processes along molecular wires based on phenylenevinylene oligomers: a quantum-chemical insight," *Journal of the American Chemical Society*, vol. 124, no. 16, pp. 4436-4447, 2002.
- [8] T. J. Dale and J. Rebek Jr., "Fluorescent sensors for organophosphorus nerve agent mimics," *Journal of the American Chemical Society*, vol. 128, no. 14, pp. 4500-4501, 2006.
- [9] I. D. Petsalakis, I. S. K. Kerkines, N. N. Lathiotakis, and G. Theodorakopoulos, "Emitting and electron-transfer electronic states of tertiary amine-fluorophore sensor systems," *Chemical Physics Letters*, vol. 474, no. 4-6, pp. 278-284, 2009.
- [10] S. V. Rosokha and J. K. Kochi, "Fresh look at electron-transfer mechanisms via the donor/acceptor bindings in the critical encounter complex," *Accounts of Chemical Research*, vol. 41, no. 5, pp. 641-653, 2008.
- [11] S. S. Gayathri, M. Wielopolski, E. M. Pérez et al., "Discrete supramolecular donor-acceptor complexes," *Angewandte Chemie International Edition*, vol. 48, no. 4, pp. 815-819, 2009.
- [12] J. M. Mativetsky, M. Kastler, R. C. Savage et al., "Self-assembly of a donor-acceptor dyad across multiple length scales: functional architectures for organic electronics," *Advanced Functional Materials*, vol. 19, no. 15, pp. 2486-2494, 2009.
- [13] D. Tzeli, I. D. Petsalakis, and G. Theodorakopoulos, "Electronic structure and absorption spectra of supramolecular complexes of a fullerene crown ether with a  $\pi$ -extended TTF derivative," *Physical Chemistry Chemical Physics*, vol. 13, no. 25, p. 11965, 2011.
- [14] D. Tzeli, I. D. Petsalakis, and G. Theodorakopoulos, "Molecular logic gates based on benzo-18-crown-6 ether of styrylquinoline: a theoretical study," *Physical Chemistry Chemical Physics*, vol. 18, no. 47, pp. 32132-32145, 2016.
- [15] N. N. Lathiotakis, G. Theodorakopoulos, and I. D. Petsalakis, "Electron transfer through organic molecular wires: a theoretical study," *Chemical Physics Letters*, vol. 667, pp. 45-50, 2017.
- [16] I. D. Petsalakis, G. Theodorakopoulos, O. Buchman, and R. Baer, "Applicability of Mulliken's formula for photoinduced and intramolecular charge-transfer energies," *Chemical Physics Letters*, vol. 625, pp. 98-103, 2015.
- [17] D. Tzeli, T. Mercouris, G. Theodorakopoulos, and I. D. Petsalakis, "Time-evolution study of photoinduced charge-transfer in tertiary amine-fluorophore systems," *Computational and Theoretical Chemistry*, vol. 1115, pp. 197-207, 2017.
- [18] A. G. Griesbeck, N. Hoffmann, and K.-d. Warzecha, "Photoinduced-electron-transfer chemistry: from studies on PET processes to applications in natural product synthesis," *Accounts of Chemical Research*, vol. 40, no. 2, pp. 128-140, 2007.
- [19] A. Ray, A. De, and S. Bhattacharya, "Study of energy transfer phenomenon between quantum dots and zinc porphyrin in solution," *Journal of Molecular Liquids*, vol. 246, pp. 17-24, 2017.
- [20] L. M. Arellano, L. Martín-Gomis, H. B. Gobeze et al., "Edge-on and face-on functionalized Pc on enriched semiconducting SWCNT hybrids," *Nanoscale*, vol. 10, no. 11, pp. 5205-5213, 2018.
- [21] S. Kayak, S. Paul, A. Bauri, A. Ray, and S. Bhattacharya, "Molecular assembly of PC70BM with a designed monoporphyrin: spectroscopic investigation in solution and theoretical calculations," *Journal of Molecular Liquids*, vol. 272, pp. 137-150, 2018.
- [22] J. Follana-Berná, S. Seetharaman, L. Martín-Gomis et al., "Supramolecular complex of a fused zinc phthalocyanine-zinc porphyrin dyad assembled by two imidazole-C60 units: ultrafast photoevents," *Physical Chemistry Chemical Physics*, vol. 20, no. 11, pp. 7798-7807, 2018.
- [23] A. Ray and S. Bhattacharya, "Photophysical insights behind zinc naphthalocyanine-gold nanoparticle interaction and its effect over supramolecular interaction between zinc naphthalocyanine and PyC 60 in solution," *Journal of Molecular Liquids*, vol. 232, pp. 188-194, 2017.
- [24] S. Shao, M. B. Thomas, K. H. Park, Z. Mahaffey, D. Kim, and F. D'Souza, "Sequential energy transfer followed by electron transfer in a BODIPY-bisstyrylBODIPY bound to C60 triad via a 'two-point' binding strategy," *Chemical Communications*, vol. 54, no. 1, pp. 54-57, 2018.
- [25] A. Ray, A. Bauri, and S. Bhattacharya, "Study of chemical physics on energy transfer phenomenon between quantum dots and a designed diporphyrin in solution," *Journal of Molecular Liquids*, vol. 263, pp. 64-71, 2018.
- [26] S. Seetharaman, Y. Jang, C. B. Kc, P. A. Karr, and F. D'Souza, "Peripheral phenothiazine induced suppression of charge separation from the singlet excited zinc phthalocyanine to coordinated C60 in supramolecular donor-acceptor conjugates," *Journal of Porphyrins and Phthalocyanines*, vol. 21, no. 12, pp. 870-881, 2017.
- [27] A. Ray and S. Bhattacharya, "Spectroscopic insights on energy transfer phenomenon from phthalocyanine to gold nanoparticle and role of phthalocyanine-gold nanoparticle conjugate over supramolecular interaction between fullerene and phthalocyanine in solution," *Chemical Physics Letters*, vol. 651, pp. 66-71, 2016.
- [28] E. Castro, G. Zavala, S. Seetharaman, F. D'Souza, and L. Echegoyen, "Impact of fullerene derivative isomeric purity on the performance of inverted planar perovskite solar cells," *Journal of Materials Chemistry A*, vol. 5, no. 36, pp. 19485-19490, 2017.
- [29] G. B. Schuster, "Long-range charge transfer in DNA: transient structural distortions control the distance dependence," *Accounts of Chemical Research*, vol. 33, no. 4, pp. 253-260, 2000.
- [30] F. D'Souza and O. Ito, "Photoinduced electron transfer in supramolecular systems of fullerenes functionalized with ligands capable of binding to zinc porphyrins and zinc phthalocyanines," *Coordination Chemistry Reviews*, vol. 249, no. 13-14, pp. 1410-1422, 2005.
- [31] K. Stranius, V. Iashin, T. Nikkonen, M. Muuronen, J. Helaja, and N. Tkachenko, "Effect of mutual position of electron donor and acceptor on photoinduced electron transfer in supramolecular chlorophyll-fullerene dyads," *Journal of Physical Chemistry A*, vol. 118, no. 8, pp. 1420-1429, 2014.
- [32] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, "Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science*, vol. 270, no. 5243, pp. 1789-1791, 1995.
- [33] D. Wróbel and A. Graja, "Photoinduced electron transfer processes in fullerene-organic chromophore systems," *Coordination Chemistry Reviews*, vol. 255, no. 21-22, pp. 2555-2577, 2011.
- [34] J. J. Dittmer, E. A. Marseglia, and R. H. Friend, "Electron trapping in dye/polymer blend photovoltaic cells," *Advanced Materials*, vol. 12, no. 17, pp. 1270-1274, 2000.

- [35] R. S. Mulliken, "Molecular compounds and their spectra. II," *Journal of the American Chemical Society*, vol. 74, no. 3, pp. 811–824, 1952.
- [36] R. S. Mulliken and W. B. Person, *Molecular Complexes. A Lecture and Reprint Volume*, Wiley, New York, NY, USA, 1969.
- [37] H. Taube, H. Myers, and R. L. Rich, "Observations on the mechanism of electron transfer in Solution1," *Journal of the American Chemical Society*, vol. 75, no. 16, pp. 4118–4119, 1953.
- [38] H. Taube, "Electron transfer between metal complexes: retrospective," *Science*, vol. 226, no. 4678, pp. 1028–1036, 1984.
- [39] R. A. Marcus, "On the theory of oxidation-reduction reactions involving electron transfer. I," *Journal of Chemical Physics*, vol. 24, no. 5, pp. 966–978, 1956.
- [40] R. A. Marcus, "Electron transfer reactions in chemistry: theory and experiment (nobel lecture)," *Angewandte Chemie International Edition in English*, vol. 32, no. 8, pp. 1111–1121, 1993.
- [41] N. S. Hush, "Adiabatic theory of outer sphere electron-transfer reactions in solution," *Transactions of the Faraday Society*, vol. 57, p. 557, 1961.
- [42] N. S. Hush, "Intervalence-transfer absorption. Part 2. Theoretical considerations and spectroscopic data," in *Progress in Inorganic Chemistry*, F. Albert Cotton, Ed., John Wiley, Hoboken, NJ, USA, pp. 391–444, 2007.
- [43] A. P. de Silva and N. D. McClenaghan, "Proof-of-principle of molecular-scale arithmetic," *Journal of the American Chemical Society*, vol. 122, no. 16, pp. 3965–3966, 2000.
- [44] O. A. Bozdemir, R. Guliyev, O. Buyukcakil et al., "Selective manipulation of ICT and PET processes in styryl-bodipy derivatives: applications in molecular logic and fluorescence sensing of metal ions," *Journal of the American Chemical Society*, vol. 132, no. 23, pp. 8029–8036, 2010.
- [45] H. T. Baytekin and E. U. Akkaya, "A molecular NAND gate based on Watson–Crick base pairing," *Organic Letters*, vol. 2, no. 12, pp. 1725–1727, 2000.
- [46] B. Valeur and I. Leray, "Ion-responsive supramolecular fluorescent systems based on multichromophoric calixarenes: a review," *Inorganica Chimica Acta*, vol. 360, no. 3, pp. 765–774, 2007.
- [47] P. A. de Silva, N. H. Q. Gunaratne, and C. P. McCoy, "A molecular photoionic AND gate based on fluorescent signalling," *Nature*, vol. 364, no. 6432, pp. 42–44, 1993.
- [48] S. Ozlem and E. U. Akkaya, "Thinking outside the silicon box: molecular and logic as an additional layer of selectivity in singlet oxygen generation for photodynamic therapy," *Journal of the American Chemical Society*, vol. 131, no. 1, pp. 48–49, 2009.
- [49] D. C. Magri and A. P. de Silva, "From PASS 1 to YES to AND logic: building parallel processing into molecular logic gates by sequential addition of receptors," *New Journal of Chemistry*, vol. 34, no. 3, p. 476, 2010.
- [50] M. R. Ajayakumar, G. Hundal, and P. Mukhopadhyay, "A tetrastable naphthalenediimide: anion induced charge transfer, single and double electron transfer for combinational logic gates," *Chemical Communications*, vol. 49, no. 70, p. 7684, 2013.
- [51] J. Ling, B. Daly, V. A. D. Silverson, and A. P. de Silva, "Taking baby steps in molecular logic-based computation," *Chemical Communications*, vol. 51, no. 40, pp. 8403–8409, 2015.
- [52] <http://www.optimedical.com>.
- [53] G. T. Yan, H. Li, Y. R. Zhu et al., "A highly selective colorimetric and "Off-On" fluorescent chemosensor for fluoride ions and its application as a molecular-scale logic device," *New Journal of Chemistry*, vol. 39, no. 11, pp. 8797–8801, 2015.
- [54] S. Karmakar, S. Mardanya, S. Das, and S. Baitalik, "Efficient deep-blue emitter and molecular-scale memory device based on dipyrrolyl-phenylimidazole-terpyridine assembly," *Journal of Physical Chemistry C*, vol. 119, no. 12, pp. 6793–6805, 2015.
- [55] K. Szacilowski, "Digital information processing in molecular systems," *Chemical Reviews*, vol. 108, no. 9, p. 3481, 2008.
- [56] L. M. Adleman, "Molecular computation of solutions to combinatorial problems," *Science*, vol. 266, no. 5187, p. 1021, 1994.
- [57] A. P. de Silva and N. D. McClenaghan, "Molecular-scale logic gates," *Chemistry—A European Journal*, vol. 10, no. 3, pp. 574–586, 2004.
- [58] T. H. Lee, J. I. Gonzalez, J. Zheng, and R. M. Dickson, "Single-molecule optoelectronics," *Accounts of Chemical Research*, vol. 38, no. 7, pp. 534–541, 2005.
- [59] A. P. de Silva and S. Uchiyama, "Molecular logic and computing," *Nature Nanotechnology*, vol. 2, no. 7, pp. 399–410, 2007.
- [60] U. Pischel, "Chemical approaches to molecular logic elements for addition and subtraction," *Angewandte Chemie International Edition*, vol. 46, no. 22, pp. 4026–4040, 2007.
- [61] L. B. Josefsen and R. W. Boyle, "Photodynamic therapy and the development of metal-based photosensitisers," *Metal-Based Drugs*, vol. 2008, Article ID 276109, 23 pages, 2008.
- [62] Á. T. De Baróid, C. P. McCoy, R. A. Craig et al., "Optimization of singlet oxygen production from photosensitizer-incorporated, medically relevant hydrogels," *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, vol. 105, no. 2, pp. 320–326, 2015.
- [63] C. Schweitzer and R. Schmidt, "Physical mechanisms of generation and deactivation of singlet oxygen," *Chemical Reviews*, vol. 103, no. 5, pp. 1685–1758, 2003.
- [64] A. Blázquez-Castro, "Direct 1 O 2 optical excitation: a tool for redox biology," *Redox Biology*, vol. 13, pp. 39–59, 2017.
- [65] N. Mehraban and H. S. Freeman, "Developments in PDT sensitizers for increased selectivity and singlet oxygen production," *Materials*, vol. 8, no. 7, pp. 4421–4456, 2015.
- [66] L. Benov, "Photodynamic therapy: current status and future directions," *Medical Principles and Practice*, vol. 24, no. s1, pp. 14–28, 2015.
- [67] S. B. Brown, E. A. Brown, and I. Walker, "The present and future role of photodynamic therapy in cancer treatment," *The Lancet Oncology*, vol. 5, no. 8, pp. 497–508, 2004.
- [68] R. K. Pandey and G. Zheng, "Porphyrins as photosensitizers in photodynamic therapy," in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, and R. Guilard, Eds., pp. 157–225, Academic Press, San Diego, CA, USA, 1999.
- [69] J. Schwiertz, A. Wieheb, S. Gräfe, B. Gitter, and M. Eppler, "Calcium phosphate nanoparticles as efficient carriers for photodynamic therapy against cells and bacteria," *Biomaterials*, vol. 30, no. 19, pp. 3324–3331, 2009.
- [70] K. Haedicke, D. Kozlova, S. Gräfe, U. Teichgräber, M. Eppler, and I. Hilger, "Multifunctional calcium phosphate nanoparticles for combining near-infrared fluorescence imaging and photodynamic therapy," *Acta Biomaterialia*, vol. 14, pp. 197–207, 2015.
- [71] M. Wainwright, "Non-porphyrin photosensitizers in biomedicine," *Chemical Society Reviews*, vol. 25, no. 5, p. 351, 1996.
- [72] M. Neginskaya, E. Berezhnaya, A. B. Uzdensky, and A. Y. Abramov, "Reactive oxygen species produced by a photodynamic effect induced calcium signal in neurons and

- astrocytes," *Molecular Neurobiology*, vol. 55, no. 1, pp. 96–102, 2017.
- [73] Q.-C. Zhan, X.-Q. Shi, X.-H. Yan et al., "Breaking the reduced glutathione-activated antioxidant defence for enhanced photodynamic therapy," *Journal of Materials Chemistry B*, vol. 5, no. 33, pp. 6752–6761, 2017.
- [74] A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, and K. Burgess, "BODIPY dyes in photodynamic therapy," *Chemical Society Reviews*, vol. 42, no. 1, pp. 77–88, 2013.
- [75] F. F. Sperandio, S. K. Sharma, M. Wang et al., "Photoinduced electron-transfer mechanisms for radical-enhanced photodynamic therapy mediated by water-soluble decacationic C70 and C84O2 Fullerene Derivatives," *Nanomedicine: Nanotechnology, Biology and Medicine*, vol. 9, no. 4, pp. 570–579, 2013.
- [76] W. Shao, H. Wang, S. He et al., "Photophysical properties and singlet oxygen generation of three sets of halogenated corroles," *Journal of Physical Chemistry B*, vol. 116, no. 49, pp. 14228–14234, 2012.
- [77] P. Lo, S. Wang, A. Zeug, M. Meyer, B. Röder, and D. K. P. Ng, "Preparation and photophysical properties of halogenated silicon(IV) phthalocyanines substituted axially with poly(ethylene glycol) chains," *Tetrahedron Letters*, vol. 44, no. 9, pp. 1967–1970, 2003.
- [78] L. Vachova, V. Novakova, K. Kopecky, M. Miletin, and P. Zimcik, "Effect of intramolecular charge transfer on fluorescence and singlet oxygen production of phthalocyanine analogues," *Dalton Transactions*, vol. 41, no. 38, p. 11651, 2012.



Hindawi

Submit your manuscripts at  
[www.hindawi.com](http://www.hindawi.com)

