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# FULL PAPER



# Theoretical study of the photophysical processes of a styryl-bodipy derivative eliciting an AND molecular logic gate response

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# Abstract

We study, via density functional theory and time dependent DFT calculations, the photophysical processes of a styryl-bodipy derivative, which acts as a three metalcation-receptor fluorophore and as an AND molecular logic gate in order to (a) gain information on the appropriate computational approach for successful prediction of molecular logic gate candidates, (b) rationalize the available experimental data and (c) understand how the given combination of three different receptors with the BODIPY fluorophore presents such interesting optoelectronic responses. The fluorophore (1), its monometallic complexes (1-Ca<sup>2+</sup>, 1-Zn<sup>2+</sup>, and 1-Hg<sup>2+</sup>), and its trimetallic complex (2) are studied. The calculated  $\lambda_{max}$  values for absorption and emission are in excellent agreement with experimental data. It was found that the observed quenching of emission of **1** and of the monometallic complexes is attributed to the fact that their first excited state is a charge-transfer state whereas this does not happen for the complex 2. It should be noted that for the correct ordering of the excited states, the inclusion of corrections to the excitation energies for nonequilibrium solvent effects is required; while in the case of  $1-Ca^{2+}$ , the additional explicit inclusion of the solvent is necessary for the quenching of the emission spectra.

## KEYWORDS

charge-transfer, DFT calculations, molecular logic gate, spectra, Styryl-Bodipy

# 1 | INTRODUCTION

Molecules can undergo changes in their ground or excited states, in response to modulators that can be other molecules, ions, or light of a certain wavelength.<sup>[1–8]</sup> In most cases, these changes could then be signaled by changes in the absorption or emission intensity and/or in the wavelength, and can be related to the operation of logic gates, via the familiar Boolean logic.<sup>[9]</sup> where the modulators correspond to the inputs and the observed changes correspond to the outputs.<sup>[8–14]</sup> The field of molecular logical gates (MLG) is a subject of research in many laboratories worldwide,<sup>[5,15–26]</sup> and while a great deal of the groundwork has been accomplished,<sup>[15]</sup> the field is still at an early stage in terms of practical applications.<sup>[5,15–26]</sup> However, a significant rise of information processing molecular devices is expected in the forthcoming years.<sup>[15]</sup> Theoretical studies aiming to provide experimentalists with information regarding a potential MLG candidate or to gain insight into experimental findings can play a significant role in the field of MLG.<sup>[27–31]</sup>

Photoinduced electron transfer (PET) is particularly useful, as the signal, depending on the special circumstances, is either an "on-off" or "offon" type,<sup>[32]</sup> resulting in a well-defined "digital" response: PET produces very sharp changes in the signal intensity, while keeping the emission wavelength unchanged.<sup>[9]</sup> Internal charge transfer (ICT)<sup>[33,34]</sup> on the other hand can be modulated in such a way as to generate changes in the

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absorption or emission wavelengths, which proved to be very useful for superposed logic gates, sometimes referred to as wavelengthreconfigurable logic gates.<sup>[9]</sup>

Charge-transfer states pose significant challenges to theoretical treatments. For most systems of interest, their size makes impractical the use of large-scale configuration interaction calculations and density functional theory (DFT) and time dependent DFT (TDDFT) methods are more of use, in which case care must be exercised on the particular functional employed.<sup>[35-39]</sup> For PET systems, geometry optimization of the excited state is required in order to reach the emission geometry, which is often very difficult to achieve due to interactions with other close-lying excited electronic states. Furthermore, the effect of the environment, such as the solvent, needs to be accounted for: state-specific treatment of the solvent is required for the excited states while explicit inclusion of solvent molecules in addition to the implicit methods might be necessary.<sup>[40,41]</sup>

In the present article, we study theoretically the photophysical processes of a three-receptor fluorophore that has been characterized as a three input AND MLG candidate.<sup>[9]</sup> In the literature, other molecules have also been characterized as candidates for a three input AND MLG.<sup>[19,20]</sup> Here, we study the photophysical processes of the three-receptor fluorophore that is a styryl-bodipy derivative of its monometallic complexes, and of its trimetallic complex. Their ground state and their lowest in energy-excited states are calculated. Our results reveal the mechanism of quenching of the emission of the single fluorophore and of the monometallic complexes, while the emission of the trimetallic complex of fluorophore is retained. The main purpose of the present work is to gain information on the appropriate computational approach for successful prediction of molecular logic gate candidates, to interpret the experimental data and to explain why the given combination of three different receptors with the BODIPY fluorophore has such optoelectronic responses. As will be discussed, the present study is rather challenging, and the inclusion of the corrected linear response (cLR) correction to the energies for nonequilibrium solvent effects is necessary while the explicit addition of the solvent in the case of the monometallic complex of Ca<sup>2+</sup> is also required.

# 2 | METHODOLOGY

In the present work we study theoretically the electronic structure of **1** and the complexes of **1** with each one of the three metal cations  $M = Ca^{2+}$ ,  $Zn^{2+}$ , and  $Hg^{2+}$ , **1**- $M^{2+}$ , that is, **1**- $Ca^{2+}$ , **1**- $Zn^{2+}$ , and **1**- $Hg^{2+}$ , and the complex of **1** with all three cations, that is, **2**, see Scheme **1** and Figure **1**. **1** is comprised from a central group of boron-dipyrromethene (BODIPY), that is, dipyrromethene complexed with a disubstituted boron atom typically a BF<sub>2</sub> unit, which is a fluorescent dye. Three groups are attached to BODIPY, that is, an azacrown ether (AC), a dithia-azacrown ether (DSC), and a dipicolylamine (DPA) units, see Scheme **1**.  $Ca^{2+}$  is complexed to the AC ligand,  $Hg^{2+}$  to the DSC ligand, and  $Zn^{2+}$  to the DPA ligand (see Scheme **1** and Figure **1**).

DFT and TDDFT calculations were carried out using the B3LYP<sup>[42]</sup> and PBE0<sup>[43]</sup> functionals in conjunction with the 6-31G(d,p)<sup>[44]</sup> for H, C, O, N, S, Ca, Zn and LANL2TZ<sup>[45]</sup> basis sets for Hg in acetonitrile solvent. The applicability of the used PBE0/6-31G(d,p) method employed here has been tested previously on calculations of the absorption and emission spectra in similar systems, including complexes of crown ethers and we found that it works well, see Tzeli et al.<sup>[27]</sup> B3LYP is a widely used functional and generally works well, except for calculations on charge-separated states. In our previous studies on complexes we had contradictory conclusions about the use of the B3LYP/6-31G(d,p) method on complexes of crown ethers, see Tzeli et al.<sup>[39,46]</sup> Thus, we employed the PBE0 functional mainly, with some additional calculations employing the commonly used B3LYP functional, which is particularly good for ground-state geometry optimizations.

At first conformational analyses have been carried out using the B3LYP functional in order to calculate the most stable minimum structure for each **1**, **1-Ca**<sup>2+</sup>, **1-Zn**<sup>2+</sup>, **1-Hg**<sup>2+</sup>, and **2** species. For the lowest in-energy structure, all species were fully geometry optimized in the ground state (S<sub>0</sub>) and in the first in-energy excited singlet state (S<sub>1</sub>) in acetonitrile ( $\varepsilon$  = 35.688) solvent employing the polarizable continuum model (PCM) <sup>[47]</sup>



**SCHEME 1** Calculated structures of the **1** and **2** molecule



using both B3LYP and PBE0 functionals. We found that both functionals employed predict similar geometries for both  $S_0$  and  $S_1$  states (see later). However, we choose the PBE0 functional as the most appropriate one for the present study, because it predicts better the charge-transfer states and the correct ordering of the excited states (see later). Thus, using the PBEO all species were fully geometry optimized in the first, second, and third lowest in-energy excited singlet states, that is,  $S_1$ ,  $S_2$ , and  $S_3$ , in acetonitrile solvent.

The acetonitrile was used as a solvent in order to reproduce the experimental conditions.<sup>[9]</sup> The PCM model is divided into a solute part lying inside a cavity, surrounded by the solvent part represented as a structureless material characterized by its macroscopic properties, that is, dielectric constants and solvent radius. This method reproduces solvent effects generally well,<sup>[48]</sup> however, corrections to the calculated excitation energies for nonequilibrium solvent effects are required and for this purpose the state-specific cLR approach.<sup>[49]</sup> is employed. It might be noted that generally the geometry optimization calculations using the cLR approach are time-consuming procedures. Moreover, when the procedure included cLR approach, mainly for the charge-transfer (CT) states of the given systems, did not reach full convergence. It should be noted that our results on geometry optimization using the cLR approach for the  $S_1$  excited state of 2 shows that the geometry of the  $S_1$  state remains almost the same after the application of the cLR approach. Thus, we carried out optimization of the excited state geometries without cLR and then we conducted single point calculations with the cLR approach.

In addition to the inclusion of the solvent via the PCM method and the inclusion of the nonequilibrium solvent effects via the cLR approach. we include the solvent explicitly in order to estimate its effect on the spectra on the calculated molecular systems. The inclusion of coordinating solvent molecules explicitly has been done in accordance with the usual coordination number for each cation. The main coordination number of Ca<sup>2+</sup> is 6. of Hg<sup>2+</sup> is 2 and 3, and of Zn<sup>2+</sup> is 4. The Ca<sup>2+</sup> cation interacts with five atoms of AC, one nitrogen and four oxygen atoms, Hg<sup>2+</sup> interacts with five atoms of DSC but mainly with two, and Zn<sup>2+</sup> interacts with three atoms of DPA. Thus, for all three metal cations one ACN molecule is needed, attached to the metal, and it has been added explicitly in the calculations, (Figure 2).

It should be noted that while for the calculation of the absorption peaks the number of calculated singlet states do not affect them, on the contrary for the calculation of the emission maxima the number of calculated singlet states affects them. Note that, the data obtained by the application of the cLR approach are not affected significantly by the number of the calculated singlet states. Emission maxima values obtained when 20 singlet states or more are included in the calculation are in better agreement with the cLR corrected values that are unaffected by the number of the calculated singlet states (see emission part of Results and Discussion). So, the absorption and the emission spectra of the studied systems were calculated including up to 30 singlet-spin excited electronic states.

All calculations were performed using the Gaussian 09 program package.<sup>[50]</sup> The coordinates of all the optimum structures are included in Supporting Information, Tables 1S, 2S and 5S.

# 3 | RESULTS AND DISCUSSION

The calculated structures of the lowest minima of **1** and of the complexes  $1-Ca^{2+}$ ,  $1-Zn^{2+}$ ,  $1-Hg^{2+}$ , and **2** are shown in Figure 1. All three metal cations selectively interact with a specific ligation site of **1**.  $Ca^{2+}$  prefers to interact with the AC ligand,  $Hg^{2+}$  prefers to interact with the DSC ligand, while  $Zn^{2+}$  prefers to interact with the DPA ligand, see Scheme 1.

#### 3.1 | Geometry

Complexation of the three metals with 1 results in some geometry changes of its structure in the ground (as it is shown in Figure 1) and in the excited states. Selected geometries along with the Cartesian coordinates are given in Data S1. Both functionals employed predict similar geometries. We choose the PBEO functional as the most appropriate for the present study, because it predicts better the charge-transfer states and the correct ordering of the excited states (see below). It should be noted the two lowest excited states  $S_1$  and  $S_2$  of all calculated species are an emitting state and a CT state; their position in the spectra and their ordering in some cases is altered by inclusion of the cLR process, thus they are named as  $S_{em}$  and  $S_{CT}$  according to their character.

As shown in Table S1, in the ground (S<sub>0</sub>) state, the range of the calculated bond distances between the metals and the ligating atoms in **2** is 2.4-2.7 Å for Ca<sup>2+</sup>, 2.1-2.3 Å for Zn<sup>2+</sup>, and 2.8-4.7 Å for Hg<sup>2+</sup> as obtained by both functionals. In **1-M<sup>2+</sup>** the corresponding distances are similar. Note that, there is only one large bond distance between Hg<sup>2+</sup> and ligating atoms of about 4.7 Å in both **2** and **1-Hg<sup>2+</sup>** complexes, while the other four distances range from 2.8 to 3.4 Å (cf. Table S1). In **2(1-M<sup>2+</sup>)** the metals lie above the plane of three ligating atoms at 0.86(1.02) Å for Ca<sup>2+</sup>, 0.13(0.01) Å for Zn<sup>2+</sup>, and 1.74(2.19) Å for Hg<sup>2+</sup>. Thus, the Zn<sup>2+</sup> cation almost lies in the plane of three ligating atoms and especially so in the **1-Zn<sup>2+</sup>** complex.

It is of interest to consider the geometry at the N atoms of the ligands and, in particular, whether a tetrahedral or a planar N atom approaching the geometry of quaternary N cation is calculated. It is well established that electron-donation by N leads to a quasi-planar geometry at N.<sup>[51–53]</sup> In the uncomplexed fluorophore, system **1**, the optimum geometry of the ground state but also the corresponding geometries of the two lowest excited states,  $S_{em}$  ( $S_1$ ) and  $S_{CT}$  ( $S_2$ ), show the geometry at N of the DPA ligand is nearly tetrahedral while the geometry at N of the other two ligands, that is, AC and DSC, is nearly planar, see Table 1. Upon complexation by metal dications, the geometry at N changes: For all calculated states, the N atom in the AC ligand is tetrahedral in **1-Ca<sup>2+</sup>** and **2**, that is, the dihedral  $C_1NC_2C_3$  angle is about 125°, while in **1-Zn<sup>2+</sup>** and **1-Hg<sup>2+</sup>**, it is quasi-planar (cf. also in **1**) with a dihedral  $C_1NC_2C_3$  angle which ranges from 160 to 174°. In the DSC ligand, the N atom is quasi-planar in **1-Ca<sup>2+</sup>**, **1-Zn<sup>2+</sup>**, as in **1**, with a  $C_4NC_5C_6$  dihedral angle of about 170°; while in **2** and **1-Hg<sup>2+</sup>** with a  $C_7NC_8C_9$  dihedral angle of about 178°, while in **2** and **1-Zn<sup>2+</sup>**, as also in **1**, it is tetrahedral with a dihedral angle of about 127°. Thus, in **1** only the N in DPA ligand is tetrahedral and the N atoms in the other two ligands are quasiplanar, in **2** all N atoms of the three ligands are nearly tetrahedral.

Complexation of one metal dication may affect the geometry not only of the corresponding ligand but the other two as well. For example, complexation of  $Hg^{2+}$  at DSC leads to a more tetrahedral N at that ligand, while N of DPA becomes planar, cf. Table 1. Similarly, complexation of  $Ca^{2+}$  at the AC ligand, affects as well, the geometry at N of DPA that also becomes planar compared to its tetrahedral geometry in **1**.

The fact that the N atoms of the ligands change from tetrahedral to quasi-planar, that is, toward the geometry of quaternary N cation, shows that complexation of the ligands changes their electron-donating ability within the complex. Thus, it is very interesting that addition of the  $Ca^{2+}$  or  $Hg^{2+}$  in one ligand affects the property of the other ligands to act as electron donors. As mentioned earlier, the complexation of  $Zn^{2+}$  does not affect the properties of the other ligands. All the earlier observations are also shown at the counters and the surfaces using the electrostatic potential computed of the calculated structures of **1**, **2**, **1**-**Ca**<sup>2+</sup>, **1**-**Zn**<sup>2+</sup>, and **1**-**Hg**<sup>2+</sup> which are depicted in Figure S1.

#### 3.2 | Spectra, energetics, and molecular orbitals

The vertical excitation energies for the  $S_0 \rightarrow S_x$  absorption and for the emission maxima of the three lowest excited states, their f-values, their main excitations, and corresponding coefficients for the **1**, **1**-**M**<sup>2+</sup>, and **2** species in acetonitrile solvent are collected in Tables S3 and S4 and in Figures 3–5. The absorption and emission spectra are depicted in Figure 6 and Figures S3 and S4. It should be noted that the absorption and emission spectra of solvent acetonitrile itself is found at 110 and 133 nm, respectively, that is, far away from the main peaks of the studied species.

In Figures 3–5 and Figures S5-S7 are depicted electron density plots of the HOMO (H), HOMO-1 (H-1), HOMO-2 (H-2), LUMO (L), and LUMO+1 (L + 1) molecular orbitals (MO) involved in the main singlet excitations from the ground state (S<sub>0</sub>) to the three lowest excited states, at the S<sub>0</sub> geometry for absorption and at the corresponding optimized geometry of the excited states for emission. The H and L MO are the same for all five species and for all their three excited states, that is, they are located on dipyrromethene and on two styrenes, with the exception of the S<sub>0</sub>, S<sub>1</sub> states of **1-Hg<sup>2+</sup>** complex, where the L orbital is located mainly to Hg<sup>2+</sup>. For the H-2, H-1, and L + 1 MO, there are differences among all calculated species and different states.

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	So	S <sub>em</sub>	S <sub>CT</sub>	So	S <sub>em</sub>	S <sub>em</sub> c	So	S <sub>em</sub>	S <sub>CT</sub>	S <sub>0</sub>	S <sub>em</sub>	S <sub>CT</sub>	S <sub>0</sub>	S <sub>em</sub>	S <sub>CT</sub>	S <sub>0</sub>	S <sub>em</sub>	S <sub>CT</sub>
$C_1NC_2C_3$	161.9	161.0	174.2	124.0	127.5	127.7	128.9	128.0	176.0	160.9	160.2	174.1	162.3	162.0	162.0	124.0	124.0	125.1
C4NC5C6	170.2	172.5	168.6	169.2	171.0	173.0	168.9	171.4	168.1	170.5	172.7	168.7	145.3	154.9	147.1	134.4	147.0	154.4
C <sub>7</sub> NC <sub>8</sub> C <sub>9</sub>	128.4	128.4	128.4	177.4	178.8	179.0	134.6	179.6	128.5	125.8	126.3	129.0	177.7	177.5	176.8	126.9	128.2	127.4

<sup>a</sup>Scheme 1. <sup>b</sup>An ACN molecule interacts with complex within acetonitrile solvent, **1-Ca<sup>2+</sup>-ACN**, see Figure 2. <sup>c</sup>The second excited state also emits, it is not a CT state.

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**FIGURE 2** Calculated minimum structure of  $1-Ca^{2+}$  interacting with one acetonitrile molecule (H atoms = white, C = gray, O = red, N = blue, S = yellow, B = pink, F = cyan, and Ca = green spheres)

## 3.2.1 | Energetics

The vertical and adiabatic excitation energies with respect to the ground state and the corresponding corrected values with respect to the cLR approach are shown in Table 2. The correct ordering of the two lowest excited states, named as  $S_{em}$ , which is a state that emits and as  $S_{CT}$  which is a CT state, is shown in Table 2, under the adiabatic excitation. It is observed that the inclusion of cLR methodology changes the ordering of the two states in all cases except of  $1-Hg^{2+}$ ; while for  $1-Ca^{2+}$ , the inclusion of the interaction of a molecule of the solvent with the  $Ca^{2+}$  cation (see Figure 2) is crucial not only for the change of the ordering of the two states but also for the prediction of the CT state. Note that without the addition of the interacting acetonitrile molecule, the CT state was not found. So, after the inclusion of the cLR process, the CT state is lower than the emitting state by about 0.2 eV for 1,  $1-Ca^{2+}$ , and  $1-Zn^{2+}$  and 0.5 eV for  $1-Hg^{2+}$ , which is a much larger energy difference compared to 1,  $1-Ca^{2+}$ , and  $1-Zn^{2+}$ . Finally, for 2 the emitting state is the lowest one by 0.1 eV.

Thus, we conclude that the lowest excited state is a CT state for 1,  $1-Ca^{2+}$ ,  $1-Zn^{2+}$ , and  $1-Hg^{2+}$  resulting in quenching of their emission spectra, while for 2 the lowest excited state is an emitting state resulting in retaining of the emission spectrum. This conclusion explains the experimental findings where no emission spectra are observed for the species 1,  $1-Ca^2$ , and  $1-Zn^{2+}$ , a weak peak is observed for the  $1-Hg^{2+}$ , while an intense emission peak is observed only for 2. More details about the excitations and their character are given later.

#### 3.2.2 | Absorption spectra

The B3LYP and PBE0 results on the absorption spectra are similar and they are in good agreement with the experimental values, see Table S3. The calculated absorption  $\lambda_{max}$  PBE0(B3LYP) values of **1**, **2**, **1-Ca**<sup>2+</sup>, **1-Zn**<sup>2+</sup>, and **1-Hg**<sup>2+</sup> are 624(646), 577(623), 678(700), 629(651), and 643 (666) nm, while the corresponding experimental values<sup>[9]</sup> are 692, 626, 672, 668, and 630 nm. The inclusion of the cLR approach leads only to small changes of the PBE0(B3LYP) absorption  $\lambda_{max}$  values. The shifts of the main PBE0(B3LYP) absorption peaks with respect to the experimental values range from 0.02 to 0.20 (0.01-0.13) eV, while including the cLR approach, the corresponding shifts range from 0.03 to 0.27 (0.04-0.20) eV. The largest deviation of the calculated absorption peak is observed for **1**. It seems that B3LYP presents slightly smaller deviation from experiment than PBE0, however, PBE0 predicts better CT the states and the correct ordering of the excited states. Generally, shifts of about 0.2 eV are considered as showing very good agreement between experiment and theory.<sup>[54,55]</sup>

## 3.2.3 | Emission

For the calculation of the emission maxima, it should be noted that the number of calculated singlet states affects the calculated emission maxima. Note, that this phenomenon was not observed in the absorption spectra. Thus, in the calculation of the emission maxima, when a small number of singlets is included, up to 10 states, the resulting  $\lambda_{max}$  values are smaller than the  $\lambda_{max}$  values when more than 20 singlet states are calculated. The difference between the two  $\lambda_{max}$  values is up to 91 nm. Note, that the  $\lambda$  values remain the same when 20 or more singlet states are calculated. This shows that the interaction of a large number of states, namely 20 singlet states or more, needs to be included in order to obtain convergence. Moreover, these values are in better agreement with the cLR corrected values than the ones obtained when a small number of singlet states is included. Note, that the cLR corrected values are unaffected by the number of the calculated singlet states. Finally, it might be noted as a technical detail of the calculations, while the optimization of the first excited state of **2** resulted in an emitting state, when the complex was optimized with respect to the second excited state, which was a CT state, it was located energetically after conducting the geometry optimization below the emitting state. However, the inclusion of the cLR process results in being the CT state the second excited state and the emitting state the first excited state.

FIGURE 3 Electron density plots of the molecular orbitals involved in the excitations corresponding to the major peaks for transitions from the ground (S<sub>0</sub>) to the three lowest excited states ( $S_1$ ,  $S_2$ , and  $S_3$ ) of **1** and 1-Zn<sup>2+</sup>. The S<sub>0</sub> geometry (absorption) and the optimized geometry of the corresponding excited state (emission) are employed. Relative energies of MO, f-values, and  $\lambda_{max}$  in nm of the singlet (black solid arrows) and charge-transfer excitations (blue dash arrows) are given without and (with) inclusion of the cLR correction



Theoretically, in the case of **1** without the inclusion of the cLR correction, the emission from the first excited state is an intense peak at 676 nm and a second excited state, which is a CT state observed at 675 nm (see Figure 3). However, the inclusion of the cLR process results in the CT state being the lowest one at 801 nm, that is, first excited, and the emitting state is the second one at 650 nm. Similarly, for the **1-Zn<sup>2+</sup>** species the first excited state and the first CT state are energetically degenerate and the inclusion of the cLR process results in lowering the CT state at 701 nm, with the emitting state at 661 nm. In both **1** and **1-Zn<sup>2+</sup>**, their first excited state, after cLR, is a CT excitation that corresponds to excitations from benzoazacrown ether to dipyrromethene-styrenes group (see Figure 3). Their second excited state corresponds to excitations within the dipyrromethene and styrene groups. It should be noted that while for **1** the third excited state is an emitting state, for **1-Zn<sup>2+</sup>** the third excited state is a second CT state that corresponds to excitations from dipyrromethene/styrene groups to Zn<sup>2+</sup>-DPA unit.

In the case of  $1-Ca^{2+}$ , CT states are not found close to the first excited state, and the N atom of the AC ligand is tetrahedral in the lowest energy structure in S<sub>0</sub>, S<sub>1</sub>, and S<sub>2</sub>. However, there are local minima in these three states when the N atom obtains a quasi-planar geometry, that is, similar to the geometry of quaternary N cation. Thus, we try to find out if the explicit inclusion of a solvent molecule in addition to the PCM model will change the ordering of the excited emitting and CT states. We found that the explicit addition of one acetonitrile molecule that

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FIGURE 4 Electron density plots of the molecular orbitals involved in the excitations corresponding to the major peaks for transitions from the ground ( $S_0$ ) to the three lowest excited states (S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>) of **1-Ca<sup>2+</sup>** and **1-Ca<sup>2+</sup>** interacting with one acetonitrile molecule (1-Ca<sup>2+</sup>-ACN). The  $S_0$ geometry (absorption) and the optimized geometry of the corresponding excited state (emission) are employed. Relative energies of MO, f-values, and  $\lambda_{max}$ in nm of the singlet (black solid arrows) and charge-transfer excitations (blue dash arrows) are given without and (with) inclusion of the cLR correction



interacts with Ca<sup>2+</sup> cation (Figure 2) in the calculation, denoted by 1-Ca<sup>2+</sup>-ACN, followed by the cLR correction, leads to results in accord with the experimental findings, that is, suppression of emission. In the global minimum of the ground state of 1-Ca<sup>2+</sup>-ACN, the N atom of the AC ligand is tetrahedral as in the case of the free 1-Ca<sup>2+</sup> complex. The main peak of the absorption spectra of 1-Ca<sup>2+</sup>-ACN are shifted to higher energies by about 30 nm with respect to the free 1-Ca<sup>2+</sup>, however the general shape of the absorption spectrum does not change (see Figures S3 and S4). The 1-Ca<sup>2+</sup>-ACN calculation, without taking into account the cLR process, presents two excited states one at 719 nm and a CT at 590 nm (see Figure 4). The global minimum of the first excited state has a tetrahedral N atom, while the global minimum of the second excited state has an N atom of quasi-planar geometry (see Table 1). However, after including the cLR process the ordering of the two excited states is reversed. Within cLR process, the CT excited state has a peak at 868 nm and the emitting state has a peak at 689 nm (Figure 4), and thus the experimental absence of emission spectra of 1-Ca<sup>2+</sup> is explained. The CT excitation corresponds to an excitation from benzoazacrown ether to dipyrromethene/two

FIGURE 5 Electron density plots of the molecular orbitals involved in the excitations corresponding to the major peaks for transitions from the ground (S<sub>0</sub>) to the three lowest excited states ( $S_1$ ,  $S_2$ , and  $S_3$ ) of **1-Hg<sup>2+</sup>** and **2**. The S<sub>0</sub> geometry (absorption) and the optimized geometry of the corresponding excited state (emission) are employed. Relative energies of MO, f-values, and  $\lambda_{max}$  in nm of the singlet (black solid arrows) and charge-transfer excitations (blue dash arrows) are given without and (with) inclusion of the cLR correction



styrenes unit. To sum up, the addition of one acetonitrile molecule results in making the global minimum of the second excited state to be a CT state with an N atom of a quasi-planar geometry and the cLR process corrects the ordering of the excited states and leads this CT state to be the lowest excited state. In other words, both the explicit inclusion of solvent and the cLR process are necessary for the correct ordering of the exited states in the case of  $1-Ca^{2+}$ .

In the case of  $1-Hg^{2+}$ , even before the cLR correction the first excited state calculated at 1092 nm has a CT character (and f-value 0.0053) (see Figure 5). Experimentally a weak peak was measured at 653 nm for this system.<sup>[9]</sup> Theoretically, the peak was calculated at 695 nm (corresponding to the second excited state) and the cLR corrected value was at 665 nm, in excellent agreement with the experimental value of 653 nm<sup>[9]</sup>. The reason why a weak peak is observed experimentally here but not in **1** or the other two  $1-M^{2+}$  systems may be that while in all these cases the population of the second excited state (S<sub>2</sub>) is reduced by internal conversion to the first excited state (S<sub>1</sub>) which is the CT state, in  $1-Hg^{2+}$  the energy difference between the CT and the emitting state is 0.5 eV, larger than in the other systems (see Table 2) allowing some



Absorption spectra (S<sub>0</sub>) of the lowest in energy of 1, 2, 1-Ca<sup>2+</sup>, 1-Zn<sup>2+</sup>, and 1-Hg<sup>2+</sup> and emission spectrum of 2 (S<sub>1</sub>) in acetonitrile **FIGURE 6** solvent

TABLE 2 Vertical and adiabatic excitation energies (corrected values with respect to cLR approach) in eV of the two lowest excited states (S<sub>em</sub> and S<sub>CT</sub>) at the PBE level of theory in acetonitrile solvent of 1, 1-Ca<sup>2+</sup>, 1-Zn<sup>2+</sup>, 1-Hg<sup>2+</sup>, and 2 in acetonitrile solvent

	Vertical excitation			Adiabatic excitation	
	${f S_0}  ightarrow {f S_{em}}$	$\mathbf{S_{em}} \rightarrow \mathbf{S_0}$	$\textbf{S}_{\textbf{CT}} \rightarrow \textbf{S}_{\textbf{0}}$	$S_0  ightarrow S_{em}$	${\bf S_0} \rightarrow {\bf S_{CT}}$
1	1.99(2.06)	1.83(1.91)	1.84(1.55)	1.92(1.99)	2.00(1.71)
1-Ca <sup>2+</sup>	1.83(1.90)	1.53(1.79)	2.38(2.36)	1.71(1.87) <sup>a</sup>	2.47(2.45) <sup>a</sup>
1-Ca <sup>2+ b</sup>	1.93(2.01)	1.73(1.80)	2.10(1.43)	1.82(1.96)	2.48(1.81)
1-Zn <sup>2+</sup>	1.97(2.04)	1.81(1.88)	1.77(1.77)	1.83(1.95)	1.86(1.81)
1-Hg <sup>2+</sup>	1.93(2.00)	1.78(1.86)	1.14(1.26)	1.85(1.88)	1.51(1.42)
2	2.15(2.20)	1.91(2.00)	1.71(2.08)	2.03(2.08)	1.93(2.15)

<sup>a</sup>The second excited state of **1-Ca<sup>2+</sup>** also emits, it is not a CT state.

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<sup>b</sup>An ACN molecule interacts with the Ca<sup>2+</sup> of complex within acetonitrile solvent, **1-Ca<sup>2+</sup>-ACN**, see Figure 2.

emission to be observed from S<sub>2</sub>. Note that via internal conversion from S<sub>2</sub> to S<sub>1</sub> this peak is reduced. The S<sub>2</sub>  $\rightarrow$  S<sub>0</sub> excitation correspond to excitations within the dipyrromethene and styrene groups, while the  $S_1 \rightarrow S_0$  and  $S_3 \rightarrow S_0$  excitations are CT excitations from dipyrromethene-two styrenes to Hg<sup>2+</sup>-DSC ligand and from benzoazacrown ether to dipyrromethene and to Hg<sup>2+</sup>-DSC ligand, respectively.

In addition to the above, calculations have been carried out on the  $S_1$  and  $S_2$  states of  $1-Zn^{2+}$  and  $1-Hg^{2+}$ , with inclusion of a solvent molecule explicitly, without and with cLR (values in brackets below), for comparison. The peaks of the emitted state is at 686[661] for 1-Zn<sup>2+</sup>-ACN and 699 [670] nm for 1-Hg<sup>2+</sup>-ACN; very similar to the values of those of the complexes without the addition of an ACN molecule, namely 685[661] for 1-Zn<sup>2+</sup> and 695[665] nm for 1-Hg<sup>2+</sup>. The peaks of the CT state are at 700[989] for 1-Zn<sup>2+</sup>-ACN and 916 nm for 1-Hg<sup>2+</sup>-ACN. In the case of 1-Hg<sup>2+</sup>, it was not possible to reach convergence for the CT state, with both cLR and explicit inclusion. Thus, we observe that for 1-Zn<sup>2+</sup> and 1-Hg<sup>2+</sup>, the relative ordering of the emitted state and CT state does not change with the explicit inclusion of the solvent, that is, the first excited state is a CT state, while the second excited state emits.

For 2 the main emission peak is calculated at 649(683) nm via the PBE0(B3LYP) functionals while the experimental peak was at 656 nm, in excellent agreement with the PBEO value (see Figure 5). The corresponding cLR values are 619(718), showing differences of about 30 nm with respect the experimental values. In 2, the first and the third excited states correspond to excitations within the dipyrromethene and styrene groups, while the second excited state which is a CT excitation corresponds to excitation from dipyrromethene/two styrenes groups to Hg<sup>2+</sup>-DSC ligand (see Figure 5). Finally, it should be noted that the character of the excitation of the CT states of both 2 and 1-Hg<sup>2+</sup> is similar (see Figure 5). Moreover, the character of the excitation of the CT states of 1, 1-Ca<sup>2+</sup>, and 1-Zn<sup>2+</sup> is similar and differs from that of 2 and 1-Hg<sup>2+</sup> (cf. Figures 3–5). Thus, the presence of the  $Hg^{2+}$  is responsible for the character of the CT state of 2.

Bozdemir et al<sup>[9]</sup> have shown experimentally, that **2** is a candidate for a three-input AND molecular logic gate in the emission mode because 2 has an intense emission peak while 1 and its complexes with one or two metal dications present weak or no emission peak. The present

#### TABLE 3 Relative ordering of the excited states obtained with PCM model and cLR approach



	РСМ		cLR		
	S <sub>1</sub>	\$ <sub>2</sub>	S <sub>1</sub>	<b>S</b> <sub>2</sub>	
<b>1</b> <sup>a</sup>	emit	СТ	СТ	emit	
1-Ca <sup>2+ a</sup>	emit	emit	СТ	emit	
1-Ca <sup>2+ b</sup>	emit	СТ	СТ	emit	
1-Zn <sup>2+ a,b</sup>	emit	СТ	СТ	emit	
1-Hg <sup>2+ a,b</sup>	СТ	emit	СТ	emit	
<b>2</b> <sup>a,b</sup>	СТ	emit	emit	СТ	

Abbreviations: cLR, corrected linear response; CT, charge transfer; PCM, polarizable continuum model.

<sup>a</sup>Implicit inclusion of ACN solvent.

<sup>b</sup>Explicit inclusion of ACN solvent.

theoretical study explains the experimental findings, that is, the emission of the fluorophore and of monometallic complexes is quenched, while the emission of the trimetallic complex of fluorophore is retained.

To sum up, in the **1**, **1-Ca**<sup>2+</sup>, and **1-Zn**<sup>2+</sup> species, the benzoazacrown ether acts as an electron donor and the dipyrro-methene-two styrenes group as an electron acceptor in the CT states. On the contrary, in **1-Hg**<sup>2+</sup>, the dipyrromethene-two styrenes act as an electron donor while the  $Hg^{2+}$ -DSC ligand as an electron acceptor in the first CT state, but in the second CT state again the benzoazacrown ether act as an electron donor and the dipyrromethene-two styrenes group as an electron acceptor. Thus, the ascending ordering of the groups with respect to the capability to attract electrons is benzoazacrown ether < dipyrromethene-two styrenes <  $Hg^{2+}$ -DSC.

It should be noted that the combination of three different receptors with the BODIPY fluorophore is required in order to elicit the observed optoelectronic responses. Here, the bodipy system is connected with one PET active group (DPA) and two ICT active groups (DSC and AC). The emission in all five calculated species is always from an orbital that is mainly a bodipy-centered H orbital, to the L orbital, which is also mainly dye centered. The PET activity is expected to be linked to the presence of a DPA ligand-centered orbital above the bodipy-centered orbital, while the ICT activity is expected to be linked to the presence of a DSC or AC ligand-centered orbital above the bodipy-centered orbital. What we see here is that the CT state is from the AC ligand-centered orbital to bodipy-centered orbital for **1**, **1-Ca<sup>2+</sup>** and **1-Zn<sup>2+</sup>**, that is, the ICT activity of AC ligand is dominant. The complexation of the Hg<sup>2+</sup> metal results in a change of the character of the CT state, that is, the transfer occurs from a mainly bodipy-centered (H) orbital to DSC-Hg orbital that becomes the L orbital. However, the addition of the other two metal cations are necessary to stabilize the bodipy centered H orbital and the CT state becomes the second excited state. The ICT activity of DSC acts antagonistic to the ICT activity of AC and the PET activity of DPA. As a result, the trimetallic complex emits.

# 4 | SUMMARY AND CONCLUSIONS

In the present work, we study the photophysical processes of a styryl-bodipy derivative that acts as a three-receptor fluorophore and it is a candidate for a three-input AND molecular logic gate in the emission mode. We calculated the free molecule (1), its monometallic complexes ( $1-Ca^{2+}$ ,  $1-Zn^{2+}$ , and  $1-Hg^{2+}$ ), and its trimetallic complex with the Ca<sup>2+</sup>, Zn<sup>2+</sup>, and Hg<sup>2+</sup> cations (2). We carried out DFT and TDDFT calculations using the B3LYP and PBE0 functionals in acetonitrile solvent, including the cLR correction to the energies for nonequilibrium solvent effects.

The motivation of the present work, beyond the rationalization of the complex experimental observations, was to establish a computational procedure that will yield accurately the physics of such challenging systems, including the proper approach for accounting for the effects of the solvent.

Of interest in the present work was to explain why the emissions of the single fluorophore and of the monometallic complexes are quenched, while the emission of the trimetallic complex of **1** fluorophore (**2**) is retained.

Good agreement is found between the calculated and experimental absorption  $\lambda_{max}$  values of the five calculated species: the absorption  $\lambda_{max}$  PBE0(B3LYP)[expt] values of **1**, **2**, **1-Ca<sup>2+</sup>**, **1-Zn<sup>2+</sup>**, and **1-Hg<sup>2+</sup>** are 624(646)[692], 577(623)[626], 678(700)[672], 629(651)[668], and 643(666) [630] nm.

The main emission peak of 2 is found theoretically at 649(683) nm via the PBE0(B3LYP) functionals while the experimental peak is at 656 nm, in excellent agreement with the PBE0 value. Similarly, for  $1-Hg^{2+}$  there is excellent agreement between the calculated emission from S<sub>2</sub> at 665 nm, and the experimentally observed weak emission at 653 nm.

Regarding the emissions of the single fluorophore and of the monometallic complexes, we found that they are quenched because the first excited state is a charge-transfer state. It should be noted that the inclusion of state-specific cLR approach is necessary in order to obtain the first

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excited state as a CT state in the case of systems 1, and  $1-Zn^{2+}$ , while for  $1-Ca^{2+}$ , in addition to the cLR correction the explicit inclusion of the solvent was required in order to reveal the CT character of the first excited state (see Table 3).

Thus, we recommend, for the correct calculation of the spectra of potential molecular logic gates and in general of sensors, the inclusion of both cLR approach and explicit solvent addition. It is necessary their effects to be examined and estimated in all theoretical studies. It should be noted that the accurate calculation of the spectra will lead to a successful design and prediction of MLG and sensors candidates.

Finally, it should be added that the combination of the three different receptors with the BODIPY fluorophore is needed in order to be present for such interesting optoelectronic responses. The emission in all five species calculated is always from an orbital that is mainly a bodipycentered H orbital, to the L orbital, which is also dye-centered. Regarding the CT state, the ICT activity of AC ligand overwhelms for **1**, **1-Ca**<sup>2+</sup>, and **1-Zn**<sup>2+</sup>. The complexation of the Hg<sup>2+</sup> metal in **1** results in a change to the character of the CT state, that is, the transfer occurs from a mainly bodipy centered H orbital to DSC-Hg orbital, while the addition of the other two metals results in the stabilization of the bodipy centered H orbital and the CT state becomes the second excited state. The ICT activity of DSC acts antagonistic to ICT activity of AC and PET activity of DPA. As a result, the trimetallic complex emits.

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