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Time-evolution study of photoinduced charge-transfer in tertiary amine-fluorophore systems



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ABSTRACT

Photoinduced charge transfer in a fluorescent sensor of organophosphorus nerve agents is examined by solution of the time dependent Schrödinger equation, under the influence of an external electromagnetic field and employing potential energy curves obtained by density functional theory (DFT) and time dependent DFT (TDDFT) calculations for the ground and the excited states, respectively. The systems of interest here consist of a tertiary amine-pyrene molecule, with different numbers of CH₂ spacer units between the t-amine and the pyrene. Quenching of pyrene emission has been observed in these systems, to different extent depending on the number of spacer units, which is due to photoinduced electron transfer from the t-amine to pyrene. Here, we present a new approach based on time-evolution for the explanation of the experimental observation of the quenching of pyrene emission. In this work the inversion coordinate at nitrogen is considered as a generalized coordinate for the charge-transfer process. Vibrational levels, dipole moments and dipole transition moments of the ground, excited, and charge transfer electronic states along the inversion coordinate are computed by DFT and TDDFT calculations. The time evolution of the excitation probability between the vibrational levels of the ground state and the first excited state and the charge transfer state has been calculated for different excitation frequencies. The results are in agreement with experimental observations regarding the photoinduced electron transfer and decreasing probability for charge transfer with increasing number of CH₂ spacer units between the t-amine and the pyrene.

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1. Introduction

Intramolecular or intermolecular electron or charge transfer reactions are very important in biological processes, [1] in material science, [2] in the fabrication of optoelectronic devices, [3] in energy convention, [4,5] in chemical sensors and fluorescent probes [5–8]. In the last decades a lot of research has been conducted on the study of intramolecular electron or charge transfer between a group that acts as an electron donor and a group that acts as an electron acceptor connected by a spacer, i.e., molecular bridge [7–14].

Photoinduced electron transfer, [15-22] or PET, may be described as follows: there is a system consisting of an electron donor (D) part and an electron acceptor (A). The whole system is in the ground state. In some cases, e.g. the case of *photovoltaics*, the first step is absorption of radiation to yield an excited state corresponding to excitation of the donor part (D \rightarrow D*). Then the system is converted fully or partially to a CT state where an electron or

* Corresponding authors. *E-mail addresses*: dtzeli@eie.gr (D. Tzeli), idpet@eie.gr (I.D. Petsalakis). a part of electron charge is transferred from D* to A (D* \rightarrow D⁺-A⁻). In the case of *fluorescent sensors*, which are the systems of interest of the present work, the acceptor moiety absorbs light and emission by A* is *suppressed* by PET from D to A, see Scheme 1. Sensing involves a chemical reaction that prevents the PET process and hence enhances emission.

There are different theories aiming the treatment of and understanding of charge transfer (CT) phenomena, for a review see Ref. [15] and reference therein. Most commonly the theory of R. A. Marcus [23] for the calculation of the rates of charge transfer has been evoked over the past 50 years. This theory is based on a model of coupling between the electronic potential energy surfaces of donor and acceptor states, and application of this model would require detailed knowledge of the potential energy surfaces of the electronic states of the donor and acceptor systems, something, however, which is practically impossible to achieve for polyatomic systems, with the existing theoretical methods. The normal practice is to draw simplified schematic diagrams of the variation of energy along a one-dimensional "reaction coordinate" or a generalized coordinate, corresponding to the most critical nuclear motion accompanying the electron transfer process and proceed



Scheme 1. Photoinduced electron transfer for fluorescent sensors.

in this manner. In the present work we will follow this approach, namely by employing a one-dimensional reaction coordinate for the study of PET in a fluorescent sensor.

In our previous study, [8] we have studied via DFT and TDDFT calculations a series of tertiary amine-fluorophore systems that exhibit suppression of emission due to a photoinduced electron transfer (PET) process from amine to the fluorophore. In the case of pyrene as the fluorophore, cf. Scheme 1 below, it was shown that the PET process, indicated by a change in the character of the excited state, accompanies its geometry optimization. In agreement with the experimental observations the suppression of emission diminishes with the number of the aliphatic spacers between the amine and pyrene [7]. In Ref. [8] the geometries of the minimum structures of the ground state and of the charge transfer (CT) state were computed. Additionally, the absorption transitions from the ground to low-lying excited electronic states at the geometry of the minimum structures of the ground state and the emission transition at the minimum of the CT state were calculated at the B3LYP/def2-SVP level of theory.

Here, we present a new approach for the explanation of the suppression of emission based on time-evolution. We examine the photoinduced charge transfer in the system of interest, (Scheme 2), by solution of the time-dependent Schrödinger equation including an external electromagnetic field to simulate the absorption of light, in order to determine the evolution of the population of the charge transfer state for different exciting frequencies and for different spacer units between the t-amine and pyrene. The variation of energy along a "reaction coordinate" or a generalized coordinate, corresponding to the most critical nuclear motion for the electron transfer process will be calculated with the excitation probability of the charge transfer state obtained by time evolution calculations, described below. Here we focus on the calculation of the optimized path from the 1st excited state, corresponding to



Scheme 2. Calculated structures of the 1C-4C molecules.

absorption by pyrene, to the CT state. In our previous study [8] only the minimum energy structure of the CT state was calculated. Here we focus also on the calculation of the vibrational levels of the calculated curves and on the change of the absorption and emission spectra as well as the variation of the dipole moments along the path. The approximate model considered here is relevant to the actual process since it has been found that the important geometric feature accompanying the electron transfer is planarity at N [8].

2. Computational details

The tertiary amine alcohols of pyrene (cf. Scheme 2) having one to four CH₂ units as spacers have been computed via DFT and TDDFT calculations using the B3LYP, [24] CAM-B3LYP, [25] PBE0, [26] and M06-2X [27] functionals in conjunction with the 6-31G(d,p) basis set [28]. The four systems were fully optimized in the ground, the first excited and the CT states. It was demonstrated previously that the critical geometry variation accompanying the potential energy surface (PES) in these systems is the pyramidalization at the nitrogen atom, where a nearly planar conformation at N corresponds to the geometry of the CT state. Therefore a generalized reaction coordinate, cf. Marcus's theory for charge transfer processes, [23] is defined by the pyramidalization motion at the N atom, and more specifically the generalized coordinate here is given by the dihedral angle around the N atom which is the dihedral angle between the C₁NC₃ and C₂NC₃ planes. The potential energy curves along the generalized coordinate have been determined for the ground, the first excited and the charge transfer (CT) states, and will be discussed below. For these curves, full geometry optimization (except for the $C_1NC_3C_2$ dihedral angle) was carried out at each point.

The applicability of the B3LYP functional was tested in our previous study [8] by comparison of the theoretical results with experimental quantities, [7] also see below, and it was found to be sufficient for the calculation of the minimum energy structures in the ground and the CT state of the present system. It is well established [25] that use of the B3LYP functional yields good excitation energies except for the charge-transfer states where it leads to underestimation of the excitation energy. On the other hand, functionals more appropriate for the charge-transfer states, e.g. CAM-B3LYP, can lead to an overestimation of the excitation energies [29,30]. The applicability of B3LYP, CAM-B3LYP, PBE0 and M06-2X functionals were tested here for the pyrene molecule, see Table 1S and Fig. 1S of the Electronic Supplementary Material (ESM). The absorption spectrum of pyrene using the B3LYP functional has been calculated before [31]. A detailed study of the absorption and emission spectra of pyrene using a variety of TDDFT functionals and ab initio methodologies such as coupled cluster, multi-reference configuration interaction methodologies have been published by our group [32]. Experimentally [33] has been found that the absorption spectra of pyrene present two close lying bands, a weak first absorption band and an intense second absorption band. Both B3LYP and PBE0 predict absorption maxima in good agreement with the experiment, [33] while M06-2X and CAM-B3LYP overestimate the excitation energy values, see Table 1S of the ESM. However, B3LYP and PBE0 interchange the order of the two bands while M06-2X and CAM-B3LYP predict the correct order of the bands, but the excitation energies are overestimated. A comprehensive comparison of different theoretical approaches employed on the calculation of the lowest two electronic states of pyrene has been presented previously [32]. It is well known that there are factors that cause a certain degree of allowance or forbiddenness to absorption and emission [34]. If the planarity of the pyrene group changes slightly, the oscillator strengths and the order of the bands can change, too [34,35]. In the present study, the pyrene group of **1C-4C** is not perfectly planar and therefore the order of the two bands of pyrene can change in the **1C-4C** molecules. Indeed, experimental data [7] show that the first band in **1C** is a strong band, see below, and it is in good agreement with the data provided via all four functionals. Thus, we think that for the study of the **1C-4C** species, the PBE0 and B3LYP functionals are good choices since they yield better agreement with the experimental excitation energy (absorption maximum), [7] available only for **1C**.

Absorption (from the ground state) and emission (from the first excited electronic state) spectra were calculated via the TDDFT calculations involving up to 10 singlet-spin excited electronic states. In the present work all B3LYP, CAM-B3LYP, PBE0 and M06-2X were used. However, for the determination of the reaction paths including partial geometry optimization, we proceed as previously, [8] with the B3LYP functional because of convergence difficulties encountered with the CAM-B3LYP and M06-2X functional: Geometry optimization calculations of the excited state failed to determine the CT minimum except for that of the **1C** molecule, and even in this case, convergence difficulties were encountered.

All DFT and TDDFT calculations were performed using the Gaussian 09 program package [36]. The coordinates of all the optimum structures are included in the accompanying ESM.

Vibrational analysis was carried out for all potential energy curves determined. Subsequently, we calculated the dipole moments, the vibrational levels of the states, as well as the Franck-Condon factors and the dipole transition probabilities between the vibrational levels of ground, the first excited and the CT state. The vibrational problem was solved via our codes which are described in Ref. [37]. For the calculation of the vibrational levels, the molecules are considered as two parts, one is the tertiary amine and the other one is the pyrene and the spacers, for the calculation of the reduced mass. For the potential well 51 points were calculated by DFT and 150 additional points were obtained by spline interpolation [37]. The size of the potential energy curve was dependent on the molecule and the largest dihedral angled considered ranged from 3.36 rad (for 2C) to 3.64 rad (for **4C**), with starting point at 2.0 rad. A number ranging between 21 and 47 vibrational levels were calculated for the potential curves on the ground and the excited states of the four molecules (see below). For the calculation of the ω_e three vibrational levels were used for each case.

It should be noted that vibrational calculations based on the potentials along the one-dimentional reaction coordinate do not yield vibrational levels which might be obtained from vibrational analyses on the hypersurfaces of the full system, but as noted in the introduction, will serve in the spirit of Marcus's model of potential energy curves along a one-dimentional reaction coordinate.

Time evolution of the excitation and population of the chargetransfer state, of the aforementioned molecules interacting with monochromatic laser pulses of various intensities $(1.4 \times 10^9 - 1.4 \times 10^{11} \text{ W/cm}^2)$, durations from 100 femtoseconds (fs) to 1.2 picoseconds (ps) and frequencies (3.47 and 3.475 eV), was carried out via the solution of the corresponding time-dependent Schrödinger equations (TDSE). The accurate solution of the TDSE requires that the wavefunctions of the vibrational levels and the geometry-dependent dipole transition matrix elements between them are computed reliably in each case. This is so, because our approach involves the expansion of the overall time-dependent wavefunction over the box-normalized wavefunctions of the vibrational levels and the integration of the resulting time-dependent coupled equations. The details of the theory and of the concomitant numerical algorithms are described in Refs. [38,39].

The present approach reduces the calculation of the interaction of the different electronic states over their potential energy hypersurfaces to a calculation along a one-dimensional optimized reaction coordinate, which best describes the geometrical changes accompanying the charge-transfer process (cf. Marcus's Theory). For practical reasons it is not possible to consider the full hypersurfaces. In addition to charge-transfer processes such time-evolution calculations employing a one-dimensional model have been previously employed for different applications as well [39].

3. Results and discussion

3.1. Geometry

The lowest minimum structures of the **1C-4C** molecules are shown in Fig. 1. A conformation analysis results in the lowest in energy conformer that is depicted in Fig. 1. The geometry of the lowest minimum structure of the first excited state is almost the same as the geometry of the minimum structure of the ground state. The dihedral angle $C_1NC_3C_2$ ranges from 124 to 128° in the minimum of the ground and the first excited state and about 170° in the CT state, see Table 1. The sum of the angles $C_1NC_2 + C_2$ - $NC_3 + C_3NC_1$ in the CT minimum is about 359° which means that the N atom obtains a quasi planar geometry, i.e., geometry of quaternary N cation. This occurs because electron charge is transferred from N to pyrene.

It should be noted that all four functionals predict the same geometry for the minimum of the ground state and of the first excited state for all four studied molecules and almost the same geometry for the minimum of the CT state of the 1C molecule, see Table 1. Only the lowest in energy conformers are presented here for the ground state and the S_1 state. For the CT structure two conformers are presented, see Fig. 7S of the ESM, because different functionals predict different CT conformer as the lowest one. The energy difference between these conformers is about 0.02 eV. The CT minimum for all four molecules was calculated only with B3LYP and PBE0 and it is lying lower \sim 0.4 eV than that of the S₁ state (which is therefore a local minimum). Via the CAM-B3LYP and M06-2X functionals only the CT minimum for the 1C molecule was calculated. Furthermore the ordering of the S₁ and CT minima is reversed; using the M06-2X functional, the S₁ minimum is calculated nearly degenerate to the CT minimum, while CAM-B3LYP leads to S₁ minimum calculated at 0.18 eV lower than the CT minimum. The geometry optimizations of the CT minima for the remaining molecules were not converged with the CAM-B3LYP and M06-2X functionals. Given that the experimental data [7] on the absorption spectra of the **1C** molecule is in better (and excellent) agreement with both B3LYP and PBE0 spectra, and the convergence difficulties encountered when using the CAM-B3LYP and M06-2X, we place greater confidence on the B3LYP and PBE0 data for the present work.

In accordance with the fact that all four functionals predict the same conformer for the minimum structure for the ground and the S_1 state, the calculated dipole moments are the same. For the CT minimum, not all functionals predict the same conformer as the lowest one, and the different conformers have different dipole moments, see Table 1. The dipole moment vector of the **1C** molecule for the three (S_0 , S_1 , and CT minima) are given in the Fig. 6S of the ESM.

3.2. Absorption and emission spectra

The vertical energy differences, for $S_0 \rightarrow S_1$ absorption and for S_1 (local minimum) $\rightarrow S_0$, and $S_{CT} \rightarrow S_0$ emission maxima, the corresponding λ_{max} , and the f-values are given in Table 2. A comparison with available experimental data shows that the B3LYP energy difference for $S_0 \rightarrow S_1$ is in excellent agreement with the experimental



minima of the ground and 1st excited states

minima of CT states

Fig. 1. Minimum structures of the 1C-4C molecules. The geometry of the local minimum structure of the first excited state is nearly identical to the geometry of the minimum energy structure of the ground state.

Table 1

Adiabatic energy difference ΔE in eV, dihedral angles θ in degrees, frequencies ω in cm⁻¹ and dipole moments μ in debye at the B3LYP/6-31G(d,p) (A), CAM-B3LYP/6-31G(d,p) (B), CAM-B3LYP/6-30G(d,p) (B), CAM-B3LYP/6-30G(d,p) (B), CAM-B3LYP/6-30G(d,p) (B), CAM-B3LYP/6-3 PBE0/6-31G(d,p) (C), and M06-2X/6-31G(d,p) (D) levels of theory.^a

	Method	ΔE_{GS-S1}	ΔE_{GS-CT}	ΔE_{S1-AC}	θ_{GS}	θ_{S1}	θ_{ac}	θ_{CT}	$\Sigma \phi^b$	ω_{GS}	ω_{CT}	μ_{GS}	μ_{S1}	μ_{CT}
1C	А	3.47	3.09	0.03	124.3	125.1	131.0	170.5	359.3	331.2	172.8	2.29	2.36	1.07 ^c
	В	3.79	3.97		124.4	124.6		166.8	358.6			2.33	2.43	1.08 ^c
	С	3.56	2.95		123.9	124.5		172.0	359.5			2.36	2.43	1.13 ^c
	D	3.83	3.90		123.4	123.6		167.5	358.8			2.35	2.42	1.80 ^d
2C	А	3.46	3.14	0.02	127.0	128.4	134.1	167.1	358.7	216.2	158.5	1.94	1.99	1.87 ^c
	В	3.78			127.2	127.3						1.92	1.99	
	С	3.56	3.23		126.7	127.3		166.8	358.6			1.98	2.04	0.98 ^d
	D	3.82			129.7	129.8						2.43	2.53	
3C	Α	3.47	3.07	0.05	127.2	127.6	136.4	175.1	359.8	246.6	166.0	1.98	2.02	0.90 ^c
	В	3.79			127.4	127.4						1.96	2.02	
	С	3.56	3.27		127.0	127.3		177.1	359.9			2.02	2.06	0.92 ^c
	D	3.83			126.9	126.9						1.87	1.93	
4C	Α	3.47	3.17	0.06	126.9	126.9	135.9	167.1	358.7	227.5	188.1	1.92	1.97	1.99
	В	3.79			127.2	127.3						1.89	1.95	
	С	3.57	3.39		126.8	127.0		167.2	358.7			1.95	2.00	2.01
	D	3.83			126.7	126.8						1.82	1.88	

^a GS: minimum of the ground state, S1: minimum of the 1st excited state (local minimum), CT: minimum of the charge transfer state, AC: avoided crossing between 1st excited and CT state.

 $\phi(C_1NC_2) + \phi(C_2NC_3) + \phi(C_3NC_1)$ in the CT minimum. ^c The lowest in energy conformer is **a**, see Fig. 7S of the ESM. ^d The lowest in energy conformer is **b**, see Fig. 7S of the ESM.

Table 2

Vertical excitation energies, $\Delta E_a(eV)$, for $S_0 \rightarrow S_1$ absorption and $\Delta E_e(eV)$ for $S_{1(local minimum)} \rightarrow S_0$ emission maxima λ_{max} (nm), $S_{1(CT minimum)} \rightarrow S_0$ CT transition, λ (nm), and f-Values and their coefficient contributing to the H \rightarrow L excitation for absorption and emission of the **1C-4C** molecules at the B3LYP/6-31G(d,p) (A) and CAM-B3LYP/6-31G(d,p) (B), PBE0/6-31G(d,p) (C), and M06-2X/6-31G(d,p) (D) levels of theory; experimental data are also provided.

	Method	$S_0 \to S_1$				S _{1(Local}	$_{minimum)} \rightarrow S_{0}$	0		$S_{1(CT\ minimum)} ightarrow S_0$			
		ΔE_a	λ_{max}	f	coef.	ΔE_{e}	λ_{max}	f	coef.	ΔE_{e}	λ	f	coef.
1C	А	3.62	342.8	0.3474	0.953	3.32	373.1	0.4130	0.967	2.36	525.4	0.0016	0.996
	В	4.00	309.6	0.4012	0.910	3.57	347.6	0.5392	0.974	3.34	371.3	0.1102	0.945
	С	3.72	333.5	0.3759	0.957	3.41	363.9	0.4459	0.971	2.25	550.5	0.0061	0.994
	D	4.04	307.0	0.1369	0.518	3.61	343.4	0.5555	0.981	3.27	379.6	0.0838	0.934
expt		3.63	342										
2C	Α	3.61	343.7	0.3413	0.949	3.32	372.9	0.4067	0.966	2.48	500.9	0.0084	0.998
	В	4.00	310.0	0.3878	0.916	3.57	347.3	0.5118	0.974				
	С	3.71	334.1	0.3681	0.956	3.41	363.6	0.4366	0.973	2.59	479.1	0.0238	0.997
	D	4.03	307.5	0.2907	0.796	3.60	344.0	0.5146	0.981				
3C	Α	3.61	343.1	0.3480	0.955	3.33	372.5	0.4124	0.971	2.37	523.0	0.0001	0.999
	В	4.00	309.9	0.4032	0.924	3.57	347.2	0.5226	0.974				
	С	3.72	333.7	0.3734	0.958	3.41	363.4	0.4407	0.974	2.56	483.7	0.0001	0.999
	D	4.04	306.8	0.2956	0.783	3.61	343.3	0.5346	0.981				
4C	Α	3.62	342.8	0.3382	0.956	3.33	372.1	0.4012	0.972	2.50	495.5	0.0000	1.000
	В	4.00	309.8	0.3859	0.918	3.57	347.0	0.5078	0.974				
	С	3.72	333.4	0.3624	0.958	3.42	362.9	0.4285	0.974	2.74	453.1	0.0001	1.000
	D	4.04	306.8	0.2599	0.746	3.62	342.9	0.5203	0.980				

one [7]. The PBE0 result is also in very good agreement, while the CAM-B3LYP and M06-2X functionals lead to overestimated energy differences. The adiabatic transition energies are given in Table 1, showing that the B3LYP and the PBE0 values are in agreement, while there is a large difference with the CAM-B3LYP and M06-2X transition energy for the CT state for **1C**. As noted above, the calculations employing the CAM-B3LYP and M06-2X functionals do not converge to CT minima for **2C-4C**.

Absorption and emission spectra between the ground and first excited state of all **1C-4C** are depicted in Fig. 2 and in Figs. 2S–5S of the ESM using all four functionals and only for the lowest in

energy conformers of the S_0 , S_1 and CT states. All four molecules have similar absorption spectra as well as emission spectra from the minimum of the 1st singlet exited state, i.e., $S_{1(Local minimum)} \rightarrow S_o$ see Fig. 1 and Table 2 within a given functional. The main peak of the absorption and emission spectra corresponds to a HOMO \rightarrow LUMO (H \rightarrow L) transition calculated in UV at 343(334) and 373 (364) nm respectively with large enough oscillator strengths, i.e., they range from 0.35(0.38) to 0.41(0.45) using the B3LYP(PBE0) functionals. Experimentally, the main peak of the absorption was measured at 342 nm [7] in excellent agreement with the B3LYP data, see Table 2. The CAM-B3LYP and M06-2X values are about



Fig. 2. Absorption of the 1C-4C molecules at the B3LYP/6-31G(d,p) level of theory.

30 nm blue shifted with respect to the experimental value [7]. The oscillator strength of the $S_{1(CT \text{ minimum})} \rightarrow S_0$ CT transition is significantly smaller than the non-CT transitions, (cf. Table 2) as expected, see for instance Ref. [40,41]. Emission spectra calculated at the CT geometry are included in the ESM.

The two major peaks of the $S_0 \rightarrow S_1$ absorption, see Fig. 2, at about 343(334) nm and 269(263) nm at the B3LYP(PBE0) level of

theory, correspond to pyrene-pyrene transitions. Comparing the absorption spectra of pyrene and **1C-4C** molecules, the first and the second absorption peaks of pyrene are red shifted by 10 and 5 nm, respectively, in the **1C-4C** molecules. Comparing the $S_0 \rightarrow S_1$ absorption and for $S_{1(local \ minimum)} \rightarrow S_0$ emission spectra of **1C-4C** molecules, the first peaks are red shifted by 30, in the emission spectra. Finally, comparing the $S_{1(local \ minimum)} \rightarrow S_0$ and $S_{CT} \rightarrow S_0$



emission spectra of the **1C-4C** molecules, the major peaks correspond to pyrene-pyrene transition and they are blue shifted by about 10 nm in the $S_{CT} \rightarrow S_0$ emission spectra.

3.3. Molecular orbitals

The electron density plots of the HOMO (H), HOMO-1 (H-1) and LUMO (L) molecular orbitals (MO) involved in the $S_0 \rightarrow S_1$ excitation of the absorption and emission spectrum of the 1C-4C molecules as well as the main excitations are depicted in Fig. 3. The relative energies of MO are given in parentheses. For all species the H-1, H, and L MO orbitals are the same in the minimum of the ground and the 1st excited state. The electron densities of H-1 are located on amine, while electron densities of H and L are located on pyrene. However, in the CT minimum the H-1 and H MO orbital are interchanged and thus the s1 excitation corresponds to a CT excitation from amine to pyrene. Note that for the **4C** molecule the CT has a zero oscillator strength, and the lowest in energy feasible excitation is the s2 (H-1 \rightarrow L) from pyrene to pyrene. The 1C has the largest energy difference between H-1 and H among the molecules. Note that all functionals predict similar electron density plots of the H-1, H, L MO.

3.4. Potential energy curves and vibrational analysis

The potential energy curves of the ground and the lowest 10 singlet excited states of the **1C-4C** molecules with respect to the generalized coordinate i.e., pyramidalization of the N atom ($C_1NC_3C_2$ dihedral angle) are depicted in Fig. 4. For the potential energy curves, all ground state curves and first excited state curves are fully optimized except the $C_1NC_3C_2$ dihedral angle, which

changes in steps (eg. 0.03 rad for 1 C) to obtain the reaction coordinate. The potentials of the higher excited states (excited state 2-10) are obtained as higher roots in the optimization calculation of the first excited state. As shown in Fig. 4, series of avoided crossings exist indicating changes in character in the adiabatic electronic states. In particular, the absorbing first excited state changes character into charge transfer at 2.28 rad for the 1 C system and similarly for the **2C-4C** systems at 2.34–2.38 rad.

Focusing on the adiabatic electronic states of interest here, i.e. the ground and first excited states, vibrational calculations have been carried out and the resulting levels are sketched on the relevant potential energy curves in Fig. 5. As mentioned above, there is an avoided crossing between the 1st excited state and the CT state at $131(\sim 135)^{\circ}$. The minimum of the CT corresponds to the global minimum of the adiabatic 1st excited state. The minimum of the ground state is found at about $124(127)^{\circ}$ for the **1C**(**2C-4C**) molecules, respectively. The local minimum of the 1st excited state is found at $125(127)^{\circ}$, see Table 1. The CT minimum found at about 170° while the sum of the angles $C_1NC_2 + C_2NC_3 + C_3NC_1$ in the CT minimum is about 359° indicating that the N atom has the geometry of quaternary N cation, see Table 1.

The vibrational levels are depicted in Fig. 5 and they are also given in ESM. The vibrational levels "1" corresponds to those of the ground state, the "2" corresponds to vibrational levels of the CT minimum that are lower than the avoided crossing. The levels "3" correspond to the local minimum of the 1st excited state, while the "4" are the levels lying above the avoided crossing. We observe that for the **1C** and **2C** molecules, one "3" vibrational level exist in the well. In the **3C** molecule, two "3" levels exist and in **4C** three "3" levels exists. Note that the barrier in the avoided crossing is increased to **3C** and **4C** compared to **1C**, see Table 1. The



Fig. 4. Potential energy curves of the ground and the lowest 10 singlet excited states of the 1C-4C molecules at the B3LYP/6-31G(d,p) level of theory.



Fig. 5. Potential energy curves of the ground and the first excited state of the 1C-4C molecules. Vibrational levels are plotted at the B3LYP/6-31G(d,p) level of theory.

assignment of the vibrational levels to the different sections of potential energy curve of the first excited state have been made on the basis of the corresponding wavefunctions which have been plotted in Fig. 8S of the ESM.

It was found both experimentally and theoretically by our group (via the types of the molecular orbitals) that as more methylene units are added between the amine and the pyrene the quenching efficacy is decreased [7,8]. Here, the potential energy curves also indicate that the quenching efficacy is decreased (since there is increased barrier) as the number of methylene groups is increased. We aim to obtain a more precise determination of the charge transfer process by the time evolution calculations, described below.

The dipole moment of the molecules in the minimum geometry of the ground state and the local minimum structure of the first excited state is similar and it ranges from 1.9 to 2.4 Debye. In the CT minimum for **1C**, there is a 50% reduction of the dipole moment compared to ground state or the local minimum of the first excited state and the direction of the dipole moment vector changes, see **Table 1**. This is indicative of the change of the electron density distribution. The dipole moment curves of the **1C** and **4C** molecules with respect to the generalized coordinate are depicted in Fig. 6. The dipole moment at the crossing is smaller than those calculated at the minimum in the ground and the first excited state.

The ground to excited state transition dipole moments of the **1C** and **4C** molecules are also depicted in Fig. 6. We observe that the transition dipole moment curves indicate a number of avoided crossings (or changes in character) of the first excited state with higher excited states. Of particular interest is the avoided crossing at about 2.3 rad (**1C**) and 2.4 rad (**4C**), where the ground to 1st

excited state transition dipole moment changes rapidly as it is expected due to the avoided crossing between the 1st excited state and the CT state.

The vibrational levels supported (cf. Fig. 5) and the matrix elements of the dipole moment functions and transition dipole moment functions (of Fig. 6) over all these vibrational levels, are the input for the time-evolution calculations.

Excitation probabilities between the vibrational levels of the ground state and those of the first excited state of the 1C molecule using pulses of frequency of 3.47 eV and intensity of 5.6×10^9 W/ cm^2 over a large period of 1.2 ps is shown in Fig. 7. The frequency of 3.47 eV correspond to a photon that connects the "1" and the "3" vibrational levels, i.e., vibrational levels of the ground and the 1st excited state (local minimum). We observe that the transition is feasible. It is shown that the largest values of the excitation probability between "1" and "2" namely 0.1 are observed at about 250 and 650 fs; while it is larger between "1" and "3" than "1" and "2", and the largest values are observed at about 1000 fs, see Fig. 7. Note that, the CT state even though is not accessible initially via absorption it will be populated during the excited state relaxation [42]. The oscillations of the excitation probabilities have their origin to the resonant and almost resonant coupling of the first vibrational level of the ground state to the first one of the "3" state and to the adjacent levels of the "3", "2" and "4" states. These couplings give rise to Rabi oscillations between the aforementioned vibrational levels with various periods and amplitudes. Therefore, the total probability of the molecule to reside in each state, which is equal to the sum of the individual probabilities over the corresponding vibrational states, shows a complex pattern of oscillations.



Fig. 6. Dipole moments curves of the ground and the first excited state and ground to excited state transition dipole moments of the 1C and 4C molecules at the B3LYP/6-31G (d,p) level of theory.



Fig. 7. Excitation probability between the vibrational levels of the ground state (1) and the first excited state (2: global minimum, CT state; 3: local minimum and 4: above the avoided crossing) of the **1C** molecule for a photon of 3.47 eV.



Fig. 8. Excitation probability between the vibrational levels of the ground state (1) and the CT state (2) under the influence of an external electromagnetic field; the frequency of the pulse corresponds to the energy difference energy of the 0–0 levels of the ground state (1) and local minimum (3) of the excited state for the **1C** molecule.



Fig. 9. Excitation probability between the vibrational levels of the ground state (1) and the CT state (2) under the influence of an external electromagnetic field; the frequency of the pulse corresponds to the energy difference energy of the 0–0 levels of the ground state (1) and local minimum (3) of the excited state for the **4C** molecule.

Excitation probability from the vibrational levels of the ground state "1" to the CT state "2" for the 1C and 4C molecules subjected to laser pulses of various intensities over a period of 100 fs, are shown in Figs. 8 and 9. The frequencies of the pulses are 3.470 eV and 3.475 eV and correspond to the energy difference of the 0–0 levels of the ground state "1" and of the local minimum "3" excited state for the 1C and 4C molecules, respectively. We observe that especially for high intensities the excitation probability is an order of magnitude larger for the **1C** molecules compared to the 4C ones. The transfer of population to the CT "2" excited state is more efficient for the 1C molecules for two reasons: (i) the interaction matrix elements between the levels of the ground state "1" and of the global minimum CT "2" excited state are larger for the **1C** molecules compared to the **4C** ones, (ii) the interaction matrix elements between the levels of the CT "2" excited state and of the local minimum "3" excited state are larger for the 1C molecules compared to the 4C ones.

4. Summary and conclusions

In the present work, we study via TDDFT calculations the electronic states of the tertiary amine-pyrene molecules with an increasing number of methylene groups between pyrene and tertiary amine. These systems are fluorescent sensors for organophosphorus nerve agent mimics, where a suppression of fluorescence is found in the initial system attributed to a PET process between the amine and the pyrene fluorophore.

The novelty of the present work is the presentation of a new approach for the explanation of the experimental findings of the suppression of emission [7] based on time-evolution. We focus on the calculation of the optimized path from the 1st excited state, corresponding to absorption by pyrene, to the CT state as well as the variation of the dipole moments along the path and the calculation of the vibrational levels of the calculated curves.

We computed potential energy curves of the ground and the first excited state along the inversion coordinate at N. An avoided crossing of the first excited absorbing state is found with the CT state and we found that as the number of spacer (CH₂) units between t-amine and pyrene increases, the barrier due to the avoided crossing also increases. The dipole moment and dipole transition moment matrix elements over the supported vibrational levels of the different states were computed and were employed as input for the time evolution calculations on the transition probabilities between the vibrational levels of ground, the first excited and the CT state, under the influence of an external electromagnetic field, using pulses of various frequencies and intensities. In this manner, the build-up of the population of the chargetransfer state following the absorption of radiation is obtained and described pictorially, as a function of time. The results show that the excitation probability of the CT state is larger in **1C** by an order of magnitude, compared to 4C. This is in accordance with the experimental observations of decreasing fluorescence quenching with increasing number of spacer units, [7] adding a new insight to the experimental observations.

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Appendix A. Supplementary material

Geometries, energetics, vibrational levels, potential energy curves, dipole moment curves, absorption and emission spectra, excitation probabilities for pyrene and tertiary amine-pyrene molecules at the B3LYP, CAM-B3LYP, PBE0, and M06-2X/6-31G(d, p) levels of theory are given in Table 1S–4S and are depicted in Figs. 1S–13S. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2017.06.019.

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