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Testing new chromophores for singlet fission: A computational protocol applied to 2,3-diamino-1,4-benzoquinone

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ABSTRACT

We present a computational protocol devised to test the suitability of newly proposed chromophores for singlet fission. The protocol includes two main steps: testing the basic energetic requirements by ab initio calculations and simulating the photodynamics to determine singlet fission quantum yields. We applied this protocol to 2,3-diamino-1,4-benzoquinone (DAPBQ), recently proposed as a possible chromophore for singlet fission. We determined the excitation energies of DAPBQ by second order perturbation CASPT2 and NEVPT2 calculations. Then, we optimized a possible crystal structure of DAPBQ, we identified the most favourable pair of molecules within it and we ran a simulation of the excited state dynamics for that dimer embedded in the crystal at a semiempirical QM/MM level. The results indicate that DAPBQ in the crystalline phase does not undergo singlet fission and the initially prepared singlet excited state rapidly decays to the ground state.

1. Introduction

Singlet fission is a process in which a chromophore A in an excited singlet state (S_1) transfers part of its excitation energy to a neighbouring chromophore B in the ground state (S_0) and both are converted into triplet excited states (T_1) [1,2]:

This process can be exploited to improve the efficiency of photovoltaic devices. In fact, a sensitizer capable of quantitative singlet fission may generate two charge carrier pairs per absorbed photon in a semiconductor material. In 2006 it was shown [3] that singlet fission can raise the maximum power conversion efficiency of single-junction photovoltaic devices from the Shockley-Queisser limit [4] of 33.7% to 44.4%.

In the molecular pair (hereafter called the dimer) the two triplets generated via singlet fission can combine into a pure singlet state, the $^1(T_1T_1)$ state, so the total spin can be conserved and the process is spin-allowed. Like many other spin-allowed processes, singlet fission is potentially fast and can occur on a sub-picosecond time scale [5,6].

To occur with a high yield, singlet fission must be energetically favored. For two identical chromophores ($B = A$) weakly interacting, this leads to the following energy condition:

$$\Delta E(S_1) \geq 2\Delta E(T_1) \quad (2)$$

Moreover, once Eq. (2) is fulfilled, it is desirable to reduce as much as

possible the triplet-triplet annihilation $A(T_1) + B(T_1) \rightarrow A(T_2) + B(S_0)$. This yields to the second energy condition:

$$\Delta E(T_2) > 2\Delta E(T_1) \quad (3)$$

In Eqs. (2) and (3), the energies $\Delta E(S_1)$, $\Delta E(T_1)$ and $\Delta E(T_2)$ are all differences with respect to the ground state S_0 . If the singlet fission is ultrafast, in principle it is sufficient to satisfy a “weak” version of the first requirement, Eq. (2), where $\Delta E(S_1)$ is the vertical transition energy and $\Delta E(T_1)$ is the adiabatic one. However, if the thermal equilibration of the excited chromophore is faster than the singlet fission, one must compare the adiabatic transition energies, which corresponds to a “strong” version of the inequality (2). The second requirement, Eq. (3), clearly involves adiabatic transition energies. Moreover, for photovoltaic applications the triplet adiabatic energy $\Delta E(T_1)$ must exceed the band gap of the semiconductor in use.

In this work we present a thorough analysis of the suitability of a newly proposed chromophore for singlet fission. We first determine the vertical and adiabatic transition energies of S_1 and T_1 by accurate ab initio methods, to verify whether the condition (2) is satisfied. Even if the first test is positive, the singlet fission quantum yield may be too low, because of the competition with other processes such as Internal Conversion or InterSystem Crossing in a single chromophore. To determine the quantum yields we run a computational simulation of the photodynamics for the dimer. In this work we deal with a molecular crystal, the structure of which must be determined. Then, the most favorable pair of adjacent monomers within the crystal is identified as

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Fig. 1. Molecular structure of 2,3-diamino-1,4-benzoquinone (DAPBQ).

the one with the strongest interaction between the S_1 and $^1(T_1T_1)$ states. For the simulation of the photodynamics we adopt the Surface Hopping method [7] and a QM/MM scheme [8], where the QM subsystem is the chosen dimer and the MM subsystem is the rest of the crystal.

This procedure, or variants of it, can be used to sort out chromophores that fulfill the energetic requirements and undergo singlet fission with acceptable quantum yields. Once a viable chromophore has been identified, the same analysis can be applied to improve its design, by testing the effectiveness of structural variants, of mutual orientations of the two monomers and of different embeddings.

So far, two main classes of likely singlet fission systems have been identified: (i) large even alternant hydrocarbons (such as anthracene [9], tetracene [10] and pentacene [6]) and (ii) biradicaloids [11–14]. In the present work, the system under investigation is the 2,3-diamino-1,4-benzoquinone (DAPBQ) (Fig. 1), that belongs to the class of captodatively stabilized biradicaloids. According to the *ab initio* calculations performed by Wen et al. [14], it satisfies the desired adiabatic energy criteria, Eqs. (2) and (3). In this work, we carried out CASPT2 and NEVPT2 calculations to further inspect the excitation energies of DAPBQ (see Section 2). In the same section we also present two possible crystal structures of DAPBQ, computed at DFT level. Subsequently, in Section 3 we describe the QM/MM simulation of excited state dynamics for a dimer of DAPBQ in the crystal, using a trajectory surface hopping approach.

2. *Ab initio* calculations on DAPBQ

The vertical and adiabatic excitation energies for the low-lying electronic states of DAPBQ were calculated using the second order perturbation methods CASPT2 [15,16] and NEVPT2 [17–19], with the ANO-L-VTZP [20,21] basis set. In all calculations C_2 symmetry was used. We remind that NEVPT2, just as CASPT2, is a second order perturbation treatment. NEVPT2 normally requires a larger computational effort than CASPT2, but is less affected by the intruder state problem. The CASSCF reference energies and wavefunctions were obtained in a state-specific manner, using an active space of 12 electrons and 12 orbitals (8 π and 4 σ orbitals). In the second order perturbation calculations all orbitals except the 1s cores were correlated. Ground and excited state geometries were optimized at the CASPT2/ANO-L-VTZP level of theory. All CASPT2 calculations were performed using an IPEA shift [22] of 0.25 a.u. and the MOLCAS 8.0 [23] program package. Since the CASPT2 analytical gradients are not available in MOLCAS 8.0, the geometry optimizations were run numerically. The NEVPT2 calculations were performed at the CASPT2 optimized geometries in two variants, the partially contracted (PC) and the strongly contracted (SC) scheme [17], using the MOLPRO [24] program package.

The CASPT2 optimized geometries are reported in the Supporting information (Section S2). The natural orbitals of the active space for S_0 at the optimized geometry are shown in Fig. S3. They are very similar to the active orbitals for S_0 of 2,3-dichloro-1,4-benzoquinone (Fig. S2), obtained in the benchmark calculations (see Section S1) and they do not differ qualitatively from the active orbitals for S_1 and T_1 . The first singlet and triplet excited states of DAPBQ are mainly $\pi \rightarrow \pi^*$ excitations with a significant charge transfer character. A schematic representation of the dominant electron promotions in these two states is provided in Fig. 2. In Table 1 we show the vertical and adiabatic excitation energies obtained at CASSCF, CASPT2, PC- and SC-NEVPT2 level.

From the CASPT2 results it appears that the first adiabatic energy

condition for singlet fission, Eq. (2), is not fulfilled. This is in disagreement with the results of Wen et al., who used a smaller basis set (ANO-S-VDZP) for geometry optimizations and a smaller active space (12 electrons and 10 orbitals) [14]. In particular, the CASPT2 excitation energies of S_1 obtained in the present work (vertical 2.44 eV, adiabatic 1.68 eV, see Table 1) are significantly lower with respect to the values reported in Ref. [14] (2.63 and 2.23 eV). Even when a systematic error of 0.3 eV is assumed for the adiabatic excitation energy of S_1 , as discussed in the Supporting information (Section S1.3), the condition of Eq. (2) is not satisfied by 0.5 eV.

At the PC-NEVPT2 level, while the excitation energies of T_1 (vertical 1.87 eV, adiabatic 1.23 eV, see Table 1) are in excellent agreement with the CASPT2 results, the energies for S_1 are even lower (by about 0.1 eV). Moreover, the energies obtained using the SC-NEVPT2 method, which might be considered more approximate than the PC version, do not differ significantly from the CASPT2 results. Thus, the NEVPT2 energies confirm that the “strong” version of the energy condition (2) is not satisfied.

It is worth noting that in our calculations, as well as in those performed by Wen et al. [14], the CASPT2 corrections on the CASSCF relative energies are quite large, especially for S_1 , making the CASPT2 results more uncertain. However, the excitation energies computed using the NEVPT2 method, which is generally considered more accurate than CASPT2, are in good agreement with the CASPT2 ones.

To determine a possible crystal structure for DAPBQ, which is not known experimentally, periodic DFT calculations were performed starting from two known crystal structures, those of 2,3-dimethyl-1,4-benzoquinone [25] and of 2,3-diamino-1,4-naphthoquinone [26]. The former starting point yielded the ferroelectric $P1$ structure A, shown in Fig. 3. The computed vibrational frequencies confirmed that this structure is a minimum of the potential energy surface. The crystal parameters are given in Table 2 and more details in the Supporting information (Section S3). The unit cell of 2,3-diamino-1,4-naphthoquinone is made of 12 (larger) molecules and of course the initial cell had a much larger volume than the optimized one, denoted as B (2450.28 Å³ vs 1595.38 Å³). As a consequence, in this case a considerable freedom was allowed for the search of an optimal crystal structure, which turned out to be of $P2_12_12_1$ symmetry (for more details, see Section S3). Nevertheless, structure A turned out to be more stable than B, with a difference of 0.49 kcal/mol. We therefore chose structure A for the simulations described below, although we cannot exclude that even more stable structures, possibly non ferroelectric, could be found by a more extensive search.

All periodic DFT calculations were carried out with the Crystal14 code [27], using the B3LYP functional with the Grimme dispersion correction [28] and the 6-21G basis set. A grid of $8 \times 8 \times 8$ k points in the reciprocal space, according to Pack-Monkhorst method [29], was used. In the calculations not only the atomic positions, but also the cell parameters were optimized.

3. QM/MM simulation of excited state dynamics

As shown in the preceding section, probably DAPBQ does not satisfy the energetic criterion for singlet fission. However, in view of previous results [14] at variance with ours, and considering that small modifications of the DAPBQ structure might improve its energetics, we decided to simulate the excited state dynamics of a dimer of DAPBQ in a crystalline environment.

In the simulation, we follow a quantum mechanical/molecular mechanical type (QM/MM) approach, in which two neighbouring molecules of the crystal structure are treated quantum-mechanically, while the rest of the crystal is described at the molecular mechanics level. The interaction between the QM and MM subsystems is treated using the electrostatic embedding scheme [8].

Fig. 2. Dominant electron promotions in the S_1 and T_1 states of DAPBQ. Natural orbitals of the active space for S_1 and T_1 at their equilibrium geometries are shown.

Table 1

CASSCF, CASPT2, PC- and SC-NEVPT2/ANO-L-VTZP excitation energies (in eV) of the S_1 and T_1 electronic states evaluated at CASPT2/ANO-L-VTZP optimized geometries for DAPBQ. The C_2 symmetry was used. The CASSCF, CASPT2, PC- and SC-NEVPT2 energies of S_0 are -489.70801 , -491.28270 , -491.26360 and -491.25480 a.u., respectively.

Method	State	Label	Geometry		
			S_0 min.	S_1 min.	T_1 min.
CASSCF	S_0	1^1A	0.00	1.01	0.85
	S_1	1^1B	4.14	3.36	3.41
	T_1	1^3B	2.73	2.60	2.46
CASPT2	S_0	1^1A	0.00	0.75	0.61
	S_1	1^1B	2.44	1.68	1.72
	T_1	1^3B	1.86	1.27	1.24
PC-NEVPT2	S_0	1^1A	0.00	0.75	0.61
	S_1	1^1B	2.34	1.53	1.58
	T_1	1^3B	1.87	1.25	1.23
SC-NEVPT2	S_0	1^1A	0.00	0.73	0.59
	S_1	1^1B	2.49	1.62	1.68
	T_1	1^3B	1.95	1.30	1.27

3.1. Parameters choice

To treat the QM dimer, the FOMO-CI [7,30] method with the PM3 [31] semiempirical Hamiltonian and a CAS-CI active space of 12 electrons in 8 orbitals were selected. The floating occupation numbers were determined using a gaussian energy width of 0.1 a.u. By default, in the FOMO method only the active MO's have fractional occupations. However, in the dynamics simulations, at some geometries we found convergence problems of the SCF procedure, that were partially overcome by adding four occupied MO's to the orbitals with floating occupation numbers, keeping the active space of 12 electrons in 8 orbitals for the CAS-CI calculation.

The vertical and adiabatic excitation energies for the S_1 and T_1 electronic states of the monomer obtained at this level of theory (using an active space of 6 electrons in 4 orbitals) are in good agreement with the CASPT2 results reported in Ref. [14]. The results obtained with

other semiempirical hamiltonians and active space choices were not as accurate as those of PM3 CAS-CI (6,4), as shown in Table S8. With the chosen semiempirical procedure, at the most relevant geometries (minima of S_0 , S_1 and T_1) one lone pair orbital of the oxygen atoms and three π orbitals are active (Fig. S5). Moreover, in line with the CASPT2 and NEVPT2 results, S_1 and T_1 are reasonably described as HOMO $\rightarrow$ LUMO $\pi \rightarrow \pi^*$ electron promotions.

For the MM subsystem we used the OPLS-AA force field [32], as implemented in the TINKER 6.3 [33] molecular modeling package. For each atom of the DAPBQ molecule an appropriate atom type was selected (see Table S9). Moreover, the atomic charges, reported in Table S10, were determined at the CAM-B3LYP/TZVP level using the CHELPG (CHarges from ELectrostatic Potentials using a Grid based method) scheme [34] with the additional constraint of reproducing the overall molecular dipole moment.

To test the force field, we performed a geometry optimization on one molecule at the MM level, using C_2 symmetry. The geometry obtained is in good agreement with the CASPT2/ANO-L-VTZP optimized ground state geometry (see Table S11).

3.2. Preparation of the system for the QM/MM simulation

Starting from the crystal structure A obtained at the B3LYP-D/6-21G level (Section 2), an MM optimization of the atomic positions in the unit cell, using periodic boundary conditions, was performed. Then, using the MM optimized crystal structure as input geometry, a molecular dynamics trajectory in a constant temperature mode, using the Berendsen thermostat algorithm, was carried out. In the dynamics a temperature of 300 K, a time step of 1 femtosecond and a total time of 10 ns were used. Moreover, periodic boundary conditions were imposed on the unit cell. The crystal structure optimization and the thermal equilibration at the molecular mechanics level were performed using the TINKER 6.3 [33] molecular modeling package.

The cluster for the QM/MM simulations was constructed by replicating a single unit cell 3 times along the a and c crystalline axes and 7 times along the b axis. In this way an approximately cubic cluster was obtained. The “cube” contains 512 molecules (8 molecules along each edge, Fig. 4). In the dynamics two neighbouring molecules in the bulk of the system were treated at the semiempirical level, while the other

Fig. 3. Unit cell of the computed crystal structure A of DAPBQ. Two different views are shown.

molecules were described using the OPLS-AA force field (Fig. 4). In order to maintain the overall crystal structure during the simulation, the coordinates of all the atoms belonging to molecules located at the surface of the cluster were kept fixed in time.

3.3. Selection of the QM dimer

In the crystal structure A computed at the DFT level (Section 2) 15 different pairs of neighbouring molecules were identified (see Section S5). In the attempt to select the dimer with the most favourable interchromophore electronic coupling for singlet fission, the following strategy was used:

- for each of the 15 dimers a single-point QM/MM calculation is performed, using the approximately cubic cluster described in Section 3.2
- the transition dipole moment $\langle S_0S_0 | \hat{\mu} | {}^1(T_1T_1) \rangle$ between the ground state S_0S_0 and the singlet combination of the two triplets state ${}^1(T_1T_1)$ is calculated
- the pair of molecules with the highest absolute value of $\langle S_0S_0 | \hat{\mu} | {}^1(T_1T_1) \rangle$ is selected.

This choice is based on the assumption that the dipole strength of the $S_0S_0 \rightarrow {}^1(T_1T_1)$ transition is a good measure of the interaction between the ${}^1(T_1T_1)$ state and the monomer singlet states. In fact, without the contribution of the monomer singlets, the transition dipole moment for the pure ${}^1(T_1T_1)$ state is zero, because the one-electron density matrix connecting S_0S_0 and ${}^1(T_1T_1)$ vanishes (see Ref. [35]). The largest contributions are those of the S_1S_0 and S_0S_1 states that are involved in the singlet fission, because they are the closest in energy to ${}^1(T_1T_1)$ and have large transition dipoles with the ground state. The absolute values of $\langle S_0S_0 | \hat{\mu} | {}^1(T_1T_1) \rangle$ for the different dimers are reported in Table S12. The highest value is associated to the QM/MM dimer shown in Fig. 4.

Fig. 4. The approximately cubic cluster for the QM/MM simulation. The QM dimer is represented with ball atoms and stick bonds, while the MM molecules are shown in simple line drawing. A different view is shown in the Supporting information (Fig. S11).

3.4. QM/MM simulation

The QM/MM simulation of the excited state dynamics was performed using a semiclassical trajectory surface hopping approach with “on the fly” semiempirical QM/MM calculation of energies and wavefunctions (DTSH method) [7,8]. The overlap decoherence correction

Table 2
Information about the calculated crystal structure A of DAPBQ.

Space group	Lattice parameters (angstroms and degrees)						Density (g/cm ³)	Unit cell energy (a.u)
	a	b	c	α	β	γ		
P1	10.208	4.957	10.208	96.18	93.25	84.21	1.797	−1965.64719

Fig. 5. Frontier molecular orbitals of the dimer.

scheme [36] was used to take into account the quantum decoherence effect in a surface hopping framework. The calculations were carried out with a development version of the MOPAC code [37] in which the DTSH dynamics and the QM/MM FOMO-CI electronic structure method were implemented.

The 5 lowest electronic singlet states of the dimer (the QM part) were included in the simulation. They are the ground state, two excited states that can be reasonably described as electron promotions $h_A \rightarrow l_A$ and $h_B \rightarrow l_B$ (Fig. 5) or their linear combinations, the singlet combination of the two triplets state, which is mainly a double excitation $h_A, h_B \rightarrow l_A, l_B$, and a charge-transfer state, which corresponds to a mixture of $h_A \rightarrow l_B$ and $h_B \rightarrow l_A$ transitions, where an electron is transferred from one QM molecule to the other (here with h_X and l_X we indicate the HOMO and LUMO orbitals of monomer X , respectively).

A ground state thermal equilibration of the QM/MM system using the Bussi-Parrinello stochastic thermostat [38] was then performed, with a temperature of 300 K, a time step of 0.1 femtoseconds and a total time of 50 picoseconds. The initial nuclear coordinates and momenta were taken from a snapshot of the thermalized MM trajectory (Section 3.2). The spectrum obtained from the QM/MM thermal equilibration on the ground state is shown in Fig. S12. Among the four lowest excited singlet states of the system, S_2 shows the highest extinction coefficient, followed by S_1 . The large difference between the strength of the S_1 and S_2 overlapping bands shows the importance of excitonic mixing. The other two transitions, $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$, which correspond to the $^1(T_1T_1)$ and charge transfer states, show very low extinction coefficients.

Initial conditions (the initial electronic state, nuclear coordinates and velocities) for 214 excited state trajectories were sampled from the phase space distribution generated in the thermal equilibration. The sampling was performed as described in [39,40]. Each state is selected according to its excitation probability which is proportional to the square of the transition dipole moment. In the sampling procedure, a transition energy window between 2 and 3.2 eV was used; this energy interval includes the entire strong band of the spectrum shown in Fig. S12. Each trajectory was stopped if both the following conditions were satisfied for a time interval of 100 femtoseconds: the trajectory is on the ground state and the energy difference with the first excited state is higher than 0.01 a.u. (~ 0.3 eV).

Fig. 6 shows the fractions of trajectories (populations) of the electronic states included in the simulation as functions of time. As can be seen, the decay of S_2 and S_3 to the lowest excited state (S_1) is very fast. After being populated by internal conversion, the S_1 state decays rapidly to the ground state (S_0). The population of S_0 can be fitted by a single exponential function $1 - e^{-t/\tau}$, with $\tau \approx 700$ fs (Fig. 6). Starting from a singly excited state, the $^1(T_1T_1)$ state is not populated before the decay of S_1 to S_0 occurs. However, our simulations indicate that, once populated, the $^1(T_1T_1)$ state is stable. In fact, one trajectory out of 214 started in a state which is mainly $^1(T_1T_1)$ with contributions from charge-transfer configurations. In this case, the decay of the initial state to S_0 did not occur and the trajectory propagated on the $^1(T_1T_1)$ state for the entire simulation time (10 ps).

Fig. 6. Fraction of trajectories on the five singlet states included in the QM/MM simulation as function of time. The red curve is fitted by an exponential function $1 - e^{-t/\tau}$, with $\tau \approx 700$ fs.

To understand whether the fast deactivation of the excited state is typical of the isolated chromophore or is caused by the interaction with the crystalline environment, the simulation of excited state dynamics for an isolated DAPBQ molecule was carried out. After a thermal equilibration on the ground state at the temperature of 300 K using the Bussi-Parrinello stochastic thermostat [38], 208 initial conditions were sampled with the procedure described in [39,40]. Only the S_1 and S_0 states were included in the dynamics. Their populations as functions of time are shown in Fig. S13. The decay of S_1 to S_0 is much slower than in the QM/MM dimer; in fact, the population of S_0 can be fitted by the function $1 - e^{-t/\tau}$, with $\tau \approx 25$ ps. Thus, the fast deactivation of the excited state in the crystal appears to be due to the interaction of the initially excited QM molecule with the surrounding ones.

Since in the computed crystal structure of DAPBQ chosen for the simulations (structure A) the molecules are hydrogen bonded, an excited state deactivation induced by hydrogen bonding or even proton transfer may explain the fast excited state decay found in the simulation. In fact, the initial state, mainly a single excitation localized on one molecule, has a significant charge-transfer character: electron density is transferred from the amino (donor) to the carbonyl (acceptor) groups, which acquire a partial negative charge. The interactions between the oxygen atoms of the initially excited molecule and the hydrogens of the neighbouring molecules are therefore even more stabilizing than in the ground state. They may lower the excited state energy, making the S_1 - S_0 energy gap very small and the internal conversion from S_1 to S_0 much faster.

To test this hypothesis, QM/MM calculations on a QM DAPBQ molecule interacting with one or two MM hydrogen atoms were performed. The QM part was treated as the isolated monomer (see Section 3.1). For the MM part, the parameters for the amine hydrogens were

Fig. 7. S_1 - S_0 energy gap as function of the hydrogen bond length shown in (a) (red line) and of the two OH distances shown in (b) (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Molecules extracted from the crystal structure. Molecules A and B form the QM subsystem, while molecule C belongs to the MM environment.

employed (see Tables S9 and S10), as in the dynamics. Starting from the geometry shown in Fig. 7a, where the QM molecule is at the equilibrium geometry of S_1 and the MM hydrogen is positioned so as to reproduce the hydrogen bond orientation in the crystal structure (Fig. 8), the distance between the MM hydrogen and the QM oxygen was varied, while the other internal coordinates of the system were fixed. At each value of the OH distance considered, the S_1 - S_0 energy gap was computed. As the OH distance decreases, the energy difference between S_1 and S_0 becomes smaller (Fig. 7, red line). If a second MM hydrogen atom is included, as illustrated in Fig. 7b, and both OH distances are varied and set to the same value in each single point calculation, the effect is much stronger (Fig. 7, green line). Starting from an energy difference of about 1 eV for $R(\text{OH}) = 3 \text{ \AA}$, when both OH distances are set to a value of 1 Å the S_1 and S_0 states are nearly degenerate.

One more evidence of the role of the hydrogen bonding in the excited state decay is the correlation between the shortening of N-H $\cdots$ O hydrogen bonds and the occurrence of surface hops. In the QM dimer, atom O1 of molecule A can form a hydrogen bond with atom H29 or H30 of molecule B (Fig. 8). We considered the shortest of these two intermolecular OH distances, $R(\text{OH})$, and we computed its mean value for the initial conditions ($t = 0$) of the 214 surface hopping trajectories, which is $\langle R(\text{OH}) \rangle = 2.35 \text{ \AA}$ with a standard deviation of 0.43 Å. Fig. 9 shows the values of $R(\text{OH})$ and the corresponding S_1 - S_0 energy gaps at the geometries of the $S_1 \rightarrow S_0$ hops. The $R(\text{OH})$ distances tend to be considerably shorter than the initial ones, especially for the hops taking

place when the excitation is localized on molecule A, which is the hydrogen bond acceptor (red dots in the plot). By restricting the average to the red dots, $\langle R(\text{OH}) \rangle = 2.07 \pm 0.35$ is obtained, i.e. the distribution of the $R(\text{OH})$ values is shifted by $-0.28 \text{ \AA}$. Quite similar results are obtained by considering the molecules B (QM) and C (MM) in Fig. 8. An intermolecular hydrogen bond can be formed between atom O17 and H45 or H46, at the QM/MM boundary. Taking as before the shortest of these two OH distances, at $t = 0$ the average is $\langle R(\text{OH}) \rangle = 2.01 \pm 0.26 \text{ \AA}$. Fig. 9 again shows that $R(\text{OH})$ tends to be shorter at the time of surface hops and the effect is more evident when the excitation is localized on molecule B, which is in this case the hydrogen bond acceptor (green dots). The average for the green dots is $\langle R(\text{OH}) \rangle = 1.75 \pm 0.17 \text{ \AA}$, with a shift of $-0.26 \text{ \AA}$. Although the N-H $\cdots$ O hydrogen bond between an MM molecule and a QM one is considerably shorter than that between two QM molecules, both appear to accelerate the decay of the S_1 state by decreasing the S_1 - S_0 energy gap.

Combining these findings with the results reported in Fig. 7, we conclude that in the excited state the molecule on which the excitation is localized tends to form stronger hydrogen bonds with the surrounding molecules than in the ground state; these interactions lead to a significant decrease of the energy difference between S_1 and S_0 and hence to a faster decay of the excited state.

In the other computed crystal structure, denoted as B in Section 2, the molecules are strongly hydrogen bonded too: $\langle R(\text{OH}) \rangle = 1.86 \pm 0.05 \text{ \AA}$ for the shortest intermolecular N-H $\cdots$ O hydrogen bond distances (see Fig. S4). Therefore, we believe that a QM/MM simulation of excited state dynamics using structure B would show a shortening of the S_1 lifetime as obtained with structure A.

4. Conclusions

We performed a full computational investigation of 2,3-diamino-1,4-benzoquinone (DAPBQ) as a candidate chromophore for singlet fission. Our study provides a complete overview of the steps needed to test the efficiency of singlet fission in a hitherto unknown molecule. It includes preliminary CASPT2 and NEVPT2 calculations, the determination of a plausible crystal structure for this molecule, the individuation of the pair of nearest neighbours with the largest coupling between the electronic states involved in singlet fission, and a full simulation of the nonadiabatic dynamics within the crystal by the surface hopping method.

Our CASPT2 and NEVPT2 calculations indicated that, in contrast with the results of Wen et al. [14], DAPBQ does not satisfy the basic energetic criterion for singlet fission. However, the vertical excitation energy to S_1 is only slightly less than twice the adiabatic energy of T_1 , so photon absorption in the short wavelength side of the $S_0 \rightarrow S_1$ band might still provide enough energy to generate two triplet states. Moreover, even discounting the unavoidable uncertainty of the quantum chemical results, small modifications of the DAPBQ structure or of its environment might lead to more favourable energetics. Therefore, we also simulated the excited state dynamics of a dimer of DAPBQ in a crystalline environment, using the more encouraging excitation energies of S_1 and T_1 computed by Wen et al. [14] as reference values.

The outcome of the QM/MM simulation showed that in the crystalline DAPBQ fast decay to the ground state outcompetes singlet fission. Specifically, in the excited state the strengthening of the N-H $\cdots$ O intermolecular hydrogen bonds with respect to the ground state leads to a significant decrease of the energy difference between S_1 and S_0 and hence to a very fast decay of the excited state. Structural modifications of DAPBQ aimed at designing a better candidate for singlet fission should therefore prevent the formation of N-H $\cdots$ O hydrogen bonds, as well as increase slightly the difference between the T_1 and S_1 excitation energies.

Fig. 9. The S_1 - S_0 energy gap versus the $R(\text{OH})$ distance at the time of surface hops. Panel a: $R(\text{OH})$ is the shortest of the O1-H29 and O1-H30 distances. Panel b: $R(\text{OH})$ is the shortest of the O17-H45 and O17-H46 distances. For comparison, $\langle R(\text{OH}) \rangle$ and σ are also shown, i.e. respectively the mean value and the standard deviation of $R(\text{OH})$ at the beginning of the trajectories.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.chemphys.2018.07.026>.

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