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# Intermolecular Proton Shuttling in Excited State Proton Transfer Reactions : Insights from Theory

Marika Savarese<sup>1,2</sup>, Paolo A. Netti<sup>1,2</sup>, Nadia Rega<sup>1,2\*</sup>, Carlo Adamo<sup>3,4,\*</sup>, Ilaria Ciofini<sup>3</sup>

<sup>1</sup> *Dipartimento di Chimica 'Paolo Corradini', Università di Napoli Federico II, Complesso Universitario di M.S. Angelo, via Cintia, 80126 Napoli, Italy*

<sup>2</sup> *Center for Advanced Biomaterials for Health Care@CRIB, Istituto Italiano di Tecnologia, Largo Barsanti e Matteucci n, 53 80125 Napoli*

<sup>3</sup> *LECIME, Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie, UMR*

<sup>4</sup> *Institut Universitaire de France, 103 Boulevard Saint Michel, F-75005 Paris, France*

carlo-adamo@chimie-paristech.fr; phone : 0033144276728

nadia.rega@unina.it; phone : 0039081674207

## Abstract

The mechanism of base to base intermolecular proton shuttling occurring in the excited state proton transfer reaction between 7-hydroxy-4-(trifluoromethyl)coumarin (CouOH) and concentrated 1-methylimidazole base (1-MeId) in toluene solution is here disclosed by the means of a computational approach based on Density Functional Theory (DFT) and Time Dependent DFT (TD-DFT). These methods allow to characterize both the ground and excited state potential energy surfaces along the proton shuttling coordinate, and to assess the nature of the emitting species in presence of an excess of 1-MeId. As results, the tautomerism of CouOH is found to be photo-activated and, from a mechanistic point of view, the calculations clearly show that the overall driving force of the entire shuttling is the coumarin photoacidity, which is responsible both of the first proton transfer event and of the strengthening of the following chain mechanism of base to base proton hopping.

**Keywords:** ESPT, PCET, proton shuttling, DFT, TD-DFT, PCM

## 1. Introduction

Proton coupled electron transfer reactions (PCET) undoubtedly represent a mechanism of crucial importance in many systems of biological relevance, including, for instance, those responsible for nitrogen or oxygen fixation, [1-3] as well in many redox processes occurring in synthetic reactions. [4-6] For these reasons they have been the subject of many experimental and theoretical works aimed at better understanding and modeling the elementary steps of PCET processes. [7- 13]

Recently, several groups focused on the characterization of systems able to perform a coupled electron and proton transfer under irradiation, the so called Excited State Proton Transfer class of reactions (ESPT). [14-19]

Indeed, for such reactions the driving force is the change (i.e. increase) in acidity of an acidic group of a given molecule induced by irradiation (usually referred to as photoacidity), [20] which induces a spontaneous proton transfer either at the intra or intermolecular level. This type of reactions, occurring in a very fast time scale and at the excited state, can nowadays be experimentally characterized by spectroscopic measurements such as ultra fast pump-probe and time resolved emission experiments, [21] or coherent Raman methods. [22, 23]

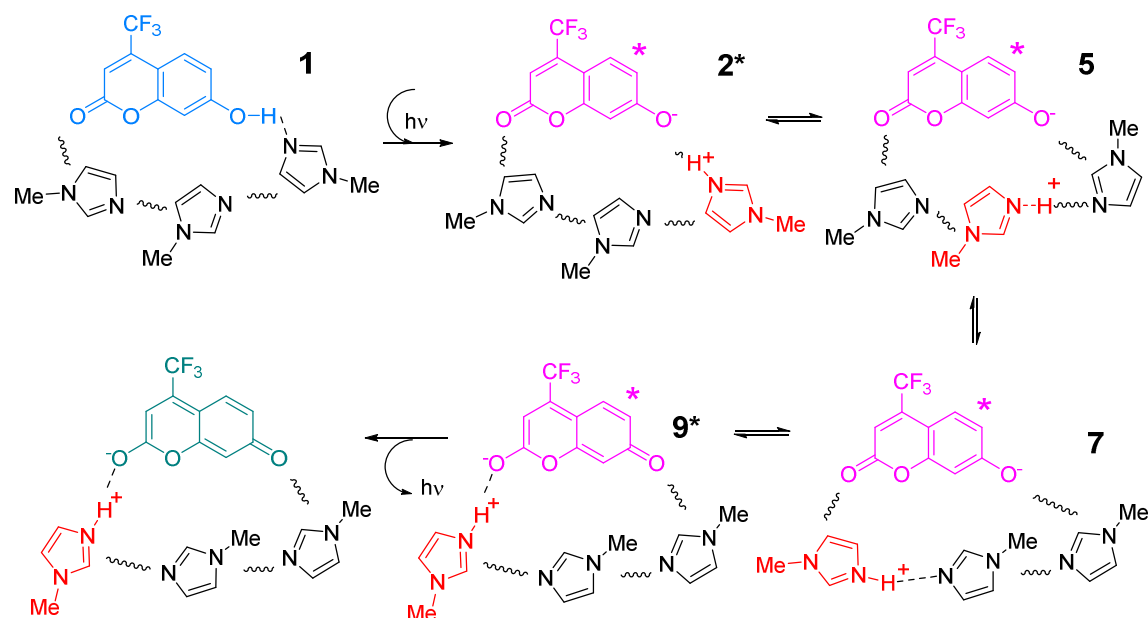
From a theoretical point of view, the full characterization of a PCET reaction claims for an accurate description of the ground and excited state potential energy surfaces (PESs) as well as, in the case of an intermolecular reaction, for a proper treatment of the intermolecular interactions and proton transfer mechanism at the excited state. Both points are far to be trivial for quantum chemical approaches especially when dealing with real systems, often large, in protic solution (such as water). Many problems also arise from the intrinsic difficulty encountered both in the choice of quantum methods able to provide a sufficiently accurate - quantitative- description of the PES and in the choice of an effective reaction coordinate since the proton motion, beside the problems related to the classical or quantum treatment of its dynamic, is accompanied to a significant electronic rearrangement and normally coupled to other nuclear degrees of freedom. [24- 27]

Not surprisingly, several papers in literature point out the strong dependence of the overall description of the mechanism on the QM model used to characterize the ES potential energy surface. [28- 35]

Indeed, recent works indicated that the approaches based on Time Dependent Density Functional Theory (TD-DFT) may represent a sufficiently accurate balance between performances and computational cost to describe excited state PES for real compounds,

[36-37, 39] and that the excited state proton transfer reaction maybe followed and described by the combined use of TD-DFT and density based indices. [39]

In this framework, using TD-DFT approaches to construct the excited state PES, we will concentrate on the accurate modeling of the intermolecular proton shuttling reactions that may occur after the initial proton transfer event to yield the final products responsible for the observed emission. In particular, we focused on the modeling of a recently accurately characterized ESPT reaction occurring between 7-hydroxy-4-(trifluoromethyl)coumarin (CouOH) and concentrated 1-methylimidazole base (1-MeId) in toluene solution (see Scheme 1). [38]



Scheme 1. Schematic ES proton transfer and shuttling mechanisms proposed for the reaction occurring between CouOH and 1-MeId at high base concentration in toluene solution. The normal form of coumarin (CouOH) is represented in light blue, its excited anionic form in violet and the tautomeric form (CouO<sub>tau</sub><sup>-</sup>) in light green. Protonated 1-MeId bases are represented in red.

For this reaction a proton shuttling mechanism, mediated by a chain of coordinating base molecules, has been experimentally proposed to justify the formation of the emissive photoproduct, characterized as the CouO<sub>tau</sub><sup>-</sup> - 1MeIdH<sup>+</sup> adduct, from the normal form of CouOH initially excited (see Scheme 1). [38]

Since in toluene the proton shuttling cannot be attributed to solvent molecules, and experimental evidences support the hypothesis that the mechanism of shuttling involves more than one base molecule and that also does not occur by simple diffusion, it is reasonable to assume that the shuttled proton is the one transferred from the normal form of the CouOH molecule as schematically depicted in Scheme 1.

In a previous theoretical study [39] the stable tautomers of the CouOH molecule (CouOH and CouOH<sub>tau</sub>) were characterized from a structural and electronic point of view in presence or in absence of one 1-MeId base, and their absorption, emission and acidic properties were successfully compared to the experimental data. [38] Furthermore the initial ESPT mechanism ruling the proton transfer from the CouOH form to the base at the excited state (first step of Scheme 1) was deeply analyzed and described in terms of density based indices. Here the possibility of using the same computational approach to describe the proton shuttling occurring while the coumarin is at the ES is disclosed further, emphasizing the good performances of TDDFT methods in the description of excited state reactivity and photochemistry.

To this aim, a minimal model able to represent the chain of imidazole molecules responsible for the proton shuttling was defined. Specifically, only three molecules of 1-MeId were explicitly considered since they represent the smallest number of molecules enabling to setup a linear chain which geometrically covers the distance between the two oxygen atoms of coumarin, as schematically depicted in Scheme 1. Even if under experimental conditions the ratio CouOH to 1-MeId is much smaller, we can assume that the present chain of base molecules represents, at least, the least energetically favored pathway for proton shuttling. Indeed, in presence of other 1-MeId molecules, energetically less expensive proton transfer pathways may be envisaged so that we can assume that the present model will provide estimation of the maximal energy requested for the proton shuttling.

## 2. Computational Details

DFT and TD-DFT were applied to model ground (GS) and excited (ES) state potential energy surfaces, respectively. When not differently stated, the global hybrid exchange correlation functional B3LYP [40] was applied for the description of both ground and excited state properties. This functional was already successfully used to characterize the absorbing and emitting species as well as the initial ESPT reaction for the same compound, and its accuracy in providing a balanced description of ground and valence excited states' structures, thermochemistry and energetics discussed in previous works. [41,42] Nonetheless, the accuracy of B3LYP in describing the proton shuttling mechanism was confirmed by supplementary TD-DFT calculations performed applying the range-separated hybrid functional CAM-B3LYP. [43] Bulk solvent effects were included by the means of the Polarizable Continuum Model (PCM) in the linear response formalism and in equilibrium regime. [44,45] All calculations were performed considering toluene as solvent, in order to allow a direct comparison with the spectroscopic experimental data. [38]

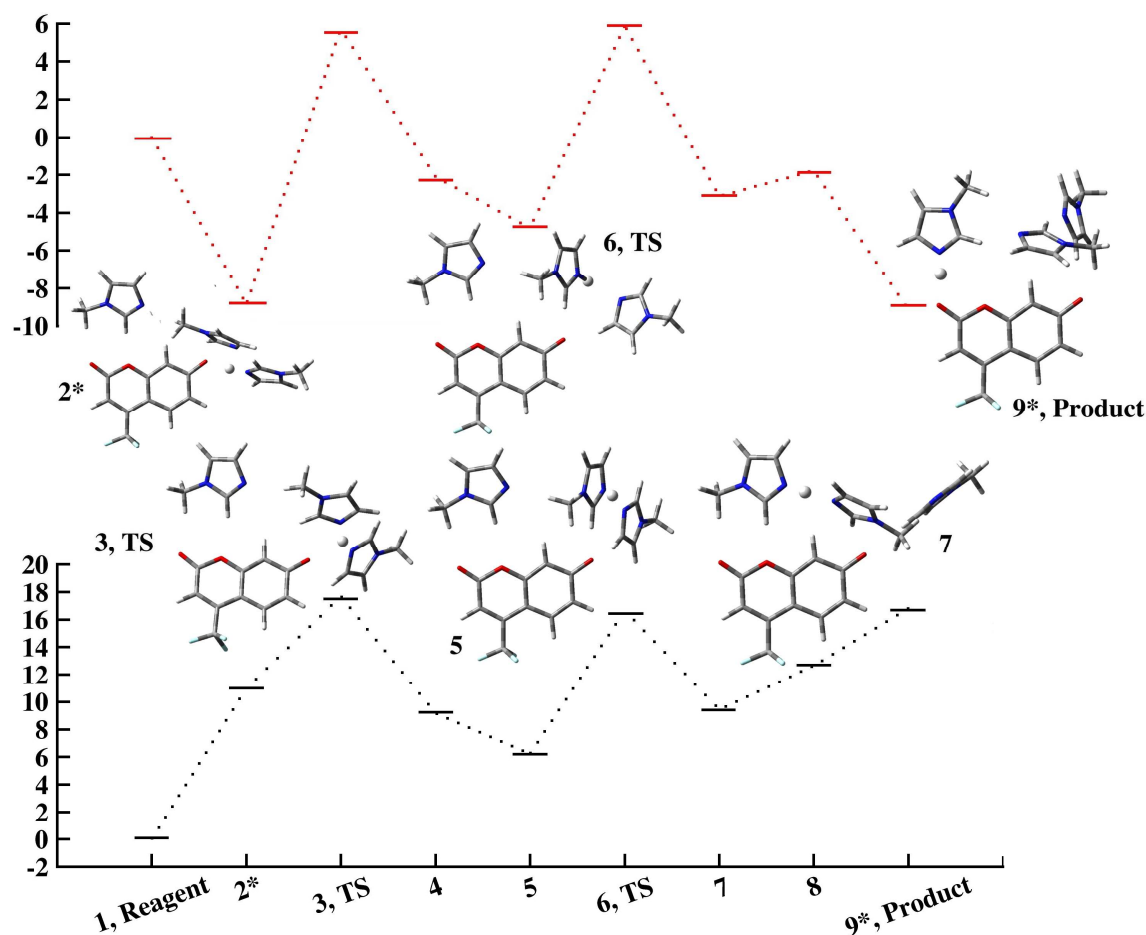
Structural optimizations were performed at the B3LYP/6-31+G(d,p)/PCM and TD-B3LYP/6-31+G(d,p)/PCM levels of theory for the ground and excited state, respectively.

Additionally, vertical excited state energies were computed at TD-CAM-B3LYP/6-31+G(d,p)/PCM level of theory. For all TD-DFT calculations at least three excited states were computed. When not differently specified structural optimizations and frequency calculations were performed at the ground state and excited states were vertically computed at TD-DFT level. All the calculations were performed by the Gaussian suite of programs. [46]

### 3. Results and Discussion

In our previous study, [39] the normal form of the coumarin molecule at the ground state was found to be 26 kcal/mol more stable than its tautomeric form. In presence of base molecules, the normal form (CouOH-(1-MeId)<sub>3</sub>, **1** in Figure 1) is still predicted to be largely more stable (of roughly 17 kcal/mol) with respect to the tautomeric form (CouOH<sub>tau</sub>-(1-MeId)<sub>3</sub>) thus confirming that, at the ground state, even in presence of an excess of base the only species present in toluene solution is predicted to be the CouOH-1-MeId adduct in agreement with experimental data. [38]

Interestingly, the introduction of further base molecules in the model does not sizably affect the H-bonding to the coumarin molecule at the ground state. Indeed, comparing the OH and NH distances computed for the CouOH-(1-MeId)<sub>3</sub> (1.02 Å and 1.63 Å) and CouOH-1-MeId (1.01 Å and 1.67 Å) adducts differences of maximum 0.04 Å can be found. The only relevant difference is that, contrary to what happens in a 1:1 adduct, in the CouOH-(1-MeId)<sub>3</sub> one the coordinated base molecule is no longer coplanar with the coumarin, due to the interaction with the next 1-MeId molecule in the base chain, with a tilt angle with respect to the CouOH plane of roughly 30°. Indeed, at the ground state, in absence of a proton transferred to the bases' chain, the neutral base to base interactions are relatively weak of the order of 6 kcal/mol so that the leading interaction is still represented by the H-bond to the coumarin molecule which is computed to be 19.6 kcal/mol. Not surprisingly, the absorption maximum computed for the CouOH-(1-MeId)<sub>3</sub> model (at 354 nm) not only very well compares with the value experimentally recorded for CouOH in presence of 1-MeId in toluene (342 nm) but it is also very similar to what previously computed for the CouOH-1-MeId adduct (347 nm). In other words, the red-shift experimentally observed when adding 1-MeId to a toluene solution of CouOH has to be ascribed to the formation of an H-bond between the CouOH and 1-MeId but not affected by the overall base concentration, that is, not quantitatively enhanced by the involvement of the 1-MeId in a base network, which is also in good agreement with the experimental data.



**Figure 1:** Computed Proton Transfer (1 to 2) and Proton Shuttling (2\* to 9\*, structures 1, 4 and 8 reported in ESI for clarity) ground (bottom) and excited (upper) state potential energy profiles. GS and ES relative energy (in kcal/mol, reagents' energy set to zero) in different scales for the sake of clarity.

Relaxation of the excited state of the CouOH-(1-MeId)<sub>3</sub> adduct yields, as expected, a proton transfer to the 1-MeId base molecule and the formation of the [CouO]<sup>\*</sup>-(1-MeIdH)<sup>+</sup>(1-MeIdH)<sub>2</sub> adduct (2\* in Figure 1), the product of the ESPT reaction and the starting point for the proton shuttling mechanism depicted in Scheme 1.

Analysis of the structural features of this adduct shows OH and HN distances (1.53 and 1.08 Å) in qualitative agreement with the results obtained with the model containing only one base molecule (1.43 and 1.12 Å) although a slightly larger OH distance is found. A slight planarization (variation of about 5° with respect to the ground state value) of the tilt angle between the coumarin and the base is also computed.

Emission from this relaxed excited state (2\* in Figure 1) is computed at 470 nm in very good agreement with the value experimentally observed at low base concentration at 460 nm, [38] and slightly red-shifted with respect to what computed with a single base molecule model



(454 nm). [39] At the ground state, energy of the  $\text{CouO}^-(1\text{-MeIdH})^+(1\text{-MeIdH})_2$  adduct vertically computed from the  $2^*$  geometry, lies 11.0 kcal/mol higher than the  $\text{CouOH}(1\text{-MeIdH})_3$  reactant, ruling out the possibility of a spontaneous PT at the GS (Figure 1). At the excited state, on the contrary, the  $[\text{CouO}^*]-(1\text{-MeIdH})^+(1\text{-MeIdH})_2$  adduct is stabilized of -8.8 kcal/mol, in agreement with the well characterized photoacidity of the CouOH molecule.

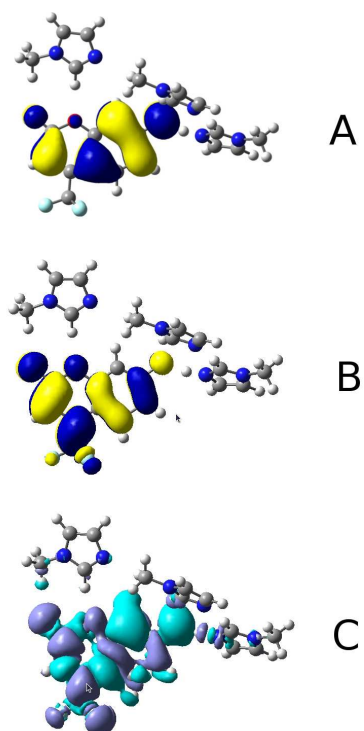


Figure 2: Contours of HOMO (A), LUMO (B), and difference in electronic density (C, positive and negative variations of density are represented in dark and light blue, respectively) involved in the initiating ESPT in the  $[\text{CouO}^*]-(1\text{-MeIdH})^+(1\text{-MeIdH})_2$  adduct. Spatial orientation of the coumarin molecule is analog to structures shown in Figure 1.

Inspection of frontier orbitals involved in the excitation (Figure 2) shows that the electronic transition involves only a reorganization of the electronic density of the CouOH molecule with a density depletion occurring on the hydroxyl moiety responsible of the photoacidity of the molecule and of the favorable deprotonation, while the imidazole bases are not directly involved in the transitions.

Starting from structure  $2^*$ , that is the excited state relaxed structure corresponding to the PT from the coumain to the first base molecule (here after  $1\text{-MeId}_A$ ), the geometry optimizations needed to fully characterize the elementary steps in the transport process have been performed considering the coumarin molecule in its ground state, in order to simplify and speed up the



calculations. The excited state profile has thus been constructed by vertically computing the energy of the first excited state on the obtained ground state geometries. Only when the proton is back transferred to the tautomeric form of the coumarin (that is for the emitting tautomeric species, **9\***), the structural features were computed considering the coumarin in its excited state, in order to correctly take into account the change in basicity/acidity of the tautomeric OH group at the excited state. For this point, the ground state energy has been computed vertically from the excited state optimized geometry. Such an optimization procedure allows for obtaining a reasonable picture of the ES profile, enabling to locate also transition states. As matter of fact it corresponds, in first approximation, to consider that the change in electronic structure upon excitation, localized on the coumarin molecule and responsible for the initial ESPT reaction, will not affect strongly the inter imidazoles proton transfer reactions (here represented by the intermediates and transition states from **3,TS** to **8**). This assumption is partially justified by the fact that the PT barriers related to the transfer between two imidazole molecules are not very sensitive to the electronic structure of the coumarin (i.e. to the fact that this molecule is computed in its ground or excited electronic state). Indeed, the barrier corresponding to the transfer from 1-MeId<sub>A</sub> to 1-MeId<sub>B</sub> (i.e. the central one in the base chain), associated to the conversion of species **5** to **7**, is practically identical on the GS (black line, Figure 1) and ES (red line, Figure 1) profiles, as also reported in Table 1. Furthermore, the base to base interaction when the proton has been transferred to the chain significantly increases, and is estimated between 26 and 56 kcal/mol, thus representing the leading interaction in the activated proton chain.

Overall inspection of Table 1 and of Figure 2, clearly shows that tautomerization reaction at the ground state is thermodynamically unfavorable (endorgonic), the product of the tautomerization reaction, CouOH<sub>tau</sub>-(1-MeId)<sub>3</sub>, lying 16.8 kcal/mol above the reagents. Furthermore, beside the unfavorable initiating proton transfer from the coumarin to the first imidazole (of 11.0 kcal/mol), the transition state associated to the proton transfer from this latter base molecule to the second (**3,TS**) is computed to be roughly 7 kcal/mol higher in energy. Overall, the initial steps of the PT reaction thus appear extremely unfavorable.

On the other hand, at the ES the stabilization of the ESPT product from the coumarin to the base (compound **2\***), computed to be -8.8 kcal/mol, determines that all the stable intermediates of the proton shuttling reactions are lying below the reactant energy (**1**), and that relevant transition states (**3,TS** and **6,TS**) are only few kcal/mol higher (in all cases less than 6 kcal/mol). Therefore, the favorable thermodynamic balance of the reaction is indeed due from one side to the photoacidity of the normal form of CouOH, leading to the formation

of the stable ESPT initial product, and to the slightly larger stability of the coumarin tautomer adduct (**9\*** of ca 1 kcal/mol more stable than **2\***) at the excited state.

While the neutral tautomeric form of the CouOH, CouOH<sub>tau</sub>-(1-MeId)<sub>3</sub>, at the ES shows O<sub>tau</sub>H and HN distances which are 1.56 and 1.07 Å, respectively, the final product of the proton shuttling (**9\***) presents both OH and ON distances that better fit to an adduct of CouO<sub>tau</sub>-(1-MeIdH<sup>+</sup>)(1-MeId)<sub>2</sub> type, in agreement with the very negative acidic constant computed for the tautomer in a previous work. [39] Emission of this species is computed in quantitative agreement with the experimental value (522 nm computed with respect to 520 nm experimentally measured [38]) thus somehow confirming the nature of product as a coumarin tautomer to protonated base adduct.

Noteworthy, this overall picture of the proton shuttling does not qualitatively change when range separated hybrids (such as CAM-B3LYP) are used to describe the ES potential energy profile, though the stabilization of the tautomer product appears more marked (Table 1).

**Table 1.** Relative energies of all species (in kcal/mol) computed at the ground and excited state at B3LYP and CAM-B3LYP level.

	GS B3LYP	ES/TD-B3LYP	ES/ TD-CAM-B3LYP
<b>1</b>	0.0	0.0	0.0
<b>2*</b>	11.0	-8.8	-5.4(-8.1) <sup>a</sup>
<b>3<sub>TS</sub></b>	17.7	5.7	4.1
<b>4</b>	9.2	-2.1	-2.8
<b>5</b>	6.2	-4.8	-5.7
<b>6<sub>TS</sub></b>	16.7	5.9	5.2
<b>7</b>	9.4	-3.1	-4.9
<b>8</b>	12.7	-1.8	-3.8
<b>9*</b>	16.8	-9.1	-7.7 (-9.8) <sup>a</sup>

\* values refer to structure optimized at the TD-B3LYP/6-31+G(d,p) level of theory.

<sup>a</sup> values refer to structure optimized at the TD-CAM-B3LYP/6-31+G(d,p) level of theory.

#### 4. Conclusions

In summary, here a general protocol for the characterization of an intermolecular excited state proton shuttling reaction based on DFT and TD-DFT is presented. As results, the tautomerism of 7-hydroxy-4-(trifluoromethyl)coumarin is found to be activated only in the excited state, as previously experimentally proven only on the basis of emission bands assignment. From a mechanistic point of view, our results clearly show that the overall driving force of the entire shuttling remains the coumarin photoacidity, which is responsible both of the first proton

transfer event and of the strengthening of the following chain mechanism of base to base proton hopping.

### **Acknowledgments**

N.R. and M.S. acknowledge the financial support from Gaussian, Inc., and MIUR, PRIN prot. 2010FM 738P\_002.

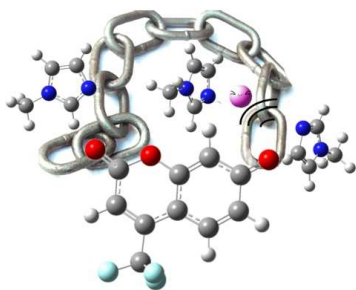
**Supplementary Electronic Information:** Structures of all 7-hydroxy-4-(trifluoromethyl)coumarin and 1-methylimidazole adducts computed.

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The mechanism of intermolecular Proton Shuttling involved in a prototypical Excited State Proton Transfer Reaction is disclosed using DFT and TD-DFT