

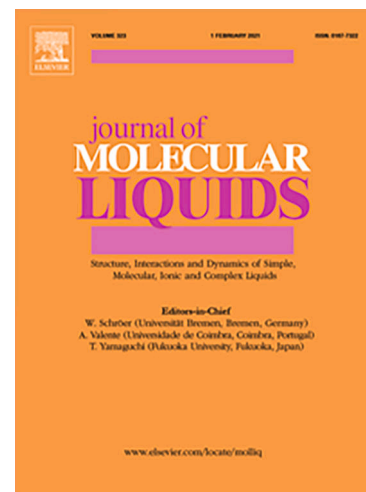
Photophysical properties of Methyl ketone based multi-responsive electrochromic materials: A theoretical investigation

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PII: S0167-7322(21)01300-3
DOI: <https://doi.org/10.1016/j.molliq.2021.116576>
Reference: MOLLIQ 116576

To appear in: *Journal of Molecular Liquids*

Received Date: 30 March 2021
Revised Date: 11 May 2021
Accepted Date: 23 May 2021



Please cite this article as: M. Erminia Alberto, B. Clara De Simone, T. Marino, N. Russo, M. Toscano, Photophysical properties of Methyl ketone based multi-responsive electrochromic materials: A theoretical investigation, *Journal of Molecular Liquids* (2021), doi: <https://doi.org/10.1016/j.molliq.2021.116576>

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Photophysical properties of Methyl ketone based multi-responsive electrochromic materials: A theoretical investigation

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Abstract

The working mechanism of a series of multi-responsive molecular switches has been investigated at atomistic level by using density functional theory (DFT) and its time dependent formulation (TDDFT). The keto-enol tautomerization has been explored considering the base assisted process, which can easily occur with a low activation energy, and also evaluating the feasibility of the electrically generation of the colored enolate form proposed in literature. Our data show that the electrically induced mechanism, consisting of a reduction followed by a proton transfer, is thermodynamically unfavorable, while a concerted proton coupled electron transfer process (PCET) can be proposed as working mechanism, resulting exergonic and able to better combine theoretical and experimental evidences.

Keyword: DFT, electrochromic materials; multicolor devices, keto-enol tautomerization, PCET

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Introduction

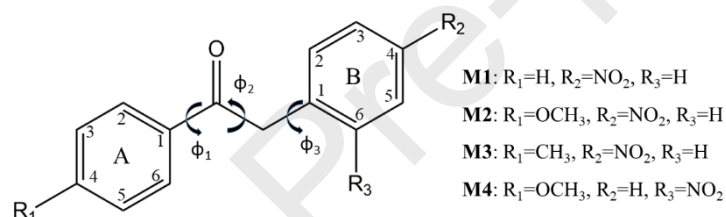
The electrochromism (EC), a phenomenon associated with the reversible change in optical properties as a result of a redox electrochemical process, has been the subject of many fundamental and applied studies since its discovery in 1961.^{1,2} Electrochromic materials display distinct visible colour changes, generally between a transparent (“bleached”) state and a coloured state, or between two coloured states.³⁻⁵ When two or more redox states are available for a class of molecules, they can exhibit different colors depending on the applied potential thus widening their field of application.^{6,7} Organic dyes materials have been subject of intensive investigations due to their ability to be switched by multiple stimuli, like application of an electric field, light irradiation, establishment of acid-base equilibria or temperature variations.^{8,9} Optical communication, multi-purpose sensors, displays, data storage devices are some examples of their current applications.¹⁰⁻¹⁷

Recently, some methyl ketones based materials have been synthesized and proposed as electrically achievable color switches, exposing them to the action of an electric field to induce the keto–enol tautomerization.^{15,16} In this new class of “electro-acid/base” dyes, the typical electrochromic properties of molecules, with low redox potential and reversible electrochemical cycle, combine with the so called pH-responsive color change by adding a strong base to the solution. Their working molecular mechanism, closely related to their degree of multi-stimuli-responsive, is not still well understood. On the basis of their experimental works on a series of substituted methyl ketone bridged color switches (**Mx**), Zhang et al.^{15,16} proposed a reaction cycle for the electrical generation of their coloured enolate form. They suggest, after the application of a proper electric field, a direct one-electron reduction of each compound **Mx** as a first step of the mechanism, with the formation of a radical ion **Mx-RA**. The latter, able to act as an “effective electro-base”, should extract a proton from a nearby neutral molecule, **Mx**, turning itself into a radical species **Mx-R** and generating, at the same time, the coloured enolate anion **Mx-A**. The loss of an electron from **Mx-R** through the reverse process generates a cationic form **Mx-C** that, by giving back a proton to the enolate **Mx-A**, restores the keto form of the compound.

A colour change from colourless to bright blue, yellow and green colours with broad absorption (500-600nm) was experimentally observed as a consequence of the electrical process of **Mx** compounds. The formation of the coloured enolate isomer **Mx-A** was proven by UV-Vis spectroscopy, IR, ¹H-NMR and GC spectroscopic analyses of both the electrically reduced and non-reduced **M1** solutions.¹⁵ Moreover, authors demonstrated as the absorption of the chemically generated enolate form of **M1** using a strong chemical base was nearly identical to that generated after being electrically reduced, further proving that the colour switch could be triggered alternately

by the electric field. In addition, on the basis of some theoretical results also presented in their work to support the thermodynamically favourable proton transfer mechanism,¹⁵ authors state that the transformation from **M1** to **M1-RA** is exergonic by 6.4 kcal mol⁻¹.

Aimed to better elucidate this interesting process at atomistic level and to provide more insights on the reaction mechanism, we have undertaken a systematic theoretical investigation turning our attention to four members of the methyl ketones family proposed by Zhang et al.¹⁵ (Scheme 1). The study has been performed employing the density functional method (DFT) previously used by our¹⁸⁻²³ and other research groups²⁴ for a series of electrochromic molecules. On the basis of the obtained structural, energetic and spectroscopic results, we show as the addition of a terbutO- base to the solution induces a fast keto-enol tautomerization process. Furthermore, concerning the electrochemical behavior, we suggest a revised mechanism based on a concerted proton coupled electron transfer (PCET) which better combine both theoretical and experimental findings.



Scheme 1. Schematic representation of the investigated compounds **M_x** (x=1-4).

Methods

Full geometry optimizations in solution have been performed employing the 6-31+G(d) basis sets and by using the B3LYP^{25,26} functional as implemented in Gaussian 09 code.²⁷ The electronic spectra of neutral and charged species have been obtained by time-dependent density functional linear response theory (TDDFT) considering the lowest twenty vertical excitation energies on previously optimized geometries at the same level of theory. Solvent effects, due to acetonitrile ($\epsilon=35.69$), have been evaluated by using the non-equilibrium procedure in the framework of polarizable continuum model.²⁸ The choice of solvent has been dictated by the presence in literature of the experimental spectra.¹⁶

IRC (intrinsic coordinate calculations) has been carried out to verify if the imaginary frequency of each transition state actually corresponds to the expected motion along the reaction coordinate.

Unrestricted calculations have been used for open-shell systems. The reported relative energies include thermodynamic corrections at 298.15 K.

Redox potentials, computed with respect to ferrocene ($E(\text{Fc}^+/\text{Fc}) = 4.29\text{V}$), have been obtained employing the Nernst equation: ²⁹

$$E = - \frac{\Delta(\Delta G_s)^{\text{redox}}}{nF}$$

where F is the Faraday constant, n is the number of electrons transferred in the reaction and $\Delta(\Delta G_{\text{solv}})^{\text{redox}}$ is the free energy variation in the Born-Haber thermodynamic cycle:

$$\Delta(\Delta G_{\text{solv}})^{\text{redox}} = \Delta G_g^{\text{redox}} + \Delta G_s(\text{Red}) - \Delta G_s(\text{Ox})$$

$\Delta G_g^{\text{redox}}$ is the change of Gibbs free energy for the reaction in gas phase and $\Delta G_s(\text{Red})$ and $\Delta G_s(\text{Ox})$ are solvation energies of reduced and oxidized species, respectively in a given redox reaction.

The value of -33.3 kcal/mol for the solvation free energy of the electron in acetonitrile³⁰ has been used for the calculation of the electron transfer processes.

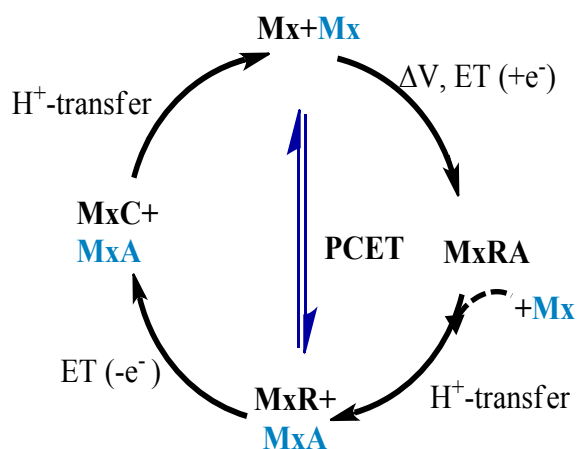
Result and discussion

Ground State and Photochemical Characterization

The reaction mechanism that should lead to the generation of the coloured enolate anion of the investigated compounds, proceeds through a one-electron reduction process triggered by the application of an external potential, followed by a subsequent proton transfer as depicted in Scheme 2. For that reason, the neutral **M1-M4** investigated compounds, take part to the working mechanism in several protonation and electronic states, properly considered in our investigation, aimed at exploring such mechanism. In particular, **M1-M4** will be referred as **Mx-R** (with x:1-4) in their radical forms, as **Mx-A** (with x:1-4) in the anionic forms, as **Mx-C** in the cationic one and as **Mx-RA**(with x:1-4) in their radical anion forms. The optimized structures of all the considered different species are reported in the Figure S1 of the Supplementary Information (SI).

The values of the main torsional angles (Φ_1 , Φ_2 and Φ_3 , Scheme 1) are given in Table 1. As it can be seen from Table 1 and from Figure S1, all neutral, radical, radical anion and cation forms of **M1**, **M2** and **M3** are characterized by two dihedral angles Φ_1 and Φ_2 which assume values very close to 180° and by the third one Φ_3 of about 90° . The anions deriving from **M1**, **M2** and **M3** differ by the value of Φ_1 that is about 150° and Φ_3 that is near to 180° while Φ_2 retains the same value as the

previous cases. The five forms of **M4** have values that differ from those of all other systems probably due to the presence of -NO₂ group in position 6 of ring B (see Scheme 1) where in the other corresponding systems there is always a hydrogen atom.



Scheme 2. One electron reduction mechanism for the investigated electrochromic processes.

Table 1. Selected angles (see Scheme 1) in degree, calculated at the B3LYP/6-31+G* level.

System	Φ_1	Φ_2	Φ_3
M1	179.9	179.7	89.6
M1-A	152.9	178.7	179.0
M1-RA	178.7	179.1	90.5
M1-R	180.0	179.8	88.7
M1-C	179.9	179.2	87.2
M2	179.8	179.0	89.8
M2-A	157.2	177.6	178.3
M2-RA	179.2	177.3	91.3
M2-R	179.8	179.8	90.3
M2-C	179.9	179.8	89.3
M3	179.5	179.5	90.3
M3-A	154.4	178.7	178.9
M3-RA	178.3	179.1	91.0
M3-R	179.5	179.6	89.3
M3-C	179.8	178.9	88.0
M4	175.4	171.4	98.2
M4-A	157.3	178.9	152.0
M4-RA	172.9	162.7	111.3
M4-R	176.6	172.3	106.7
M4-C	178.8	178.4	100.6

The computed vertical excitation energies are collected in Table 2 together with the oscillator strengths, the orbital involved in the transitions and the available experimental frequencies.

The keto neutral forms present, in all cases, a unique band at about 290 nm in agreement with the experimental measurements (about 280 nm).^[16]

Table 2. Main absorption peaks (λ in nm), oscillator strengths f and dominant transitions (H=HOMO, L=LUMO) for all the different protonation and electronic states of investigated **M1-M4** compounds, computed in Acetonitrile by using B3LYP/6-31+G*. Experimental values are taken from ref.16.

	State	λ	f	Transitions	λ_{exp}
M1	S ₁	294	0.330	H-4→L, 97%	273
	S ₂	250	0.324	H-2→L+1, 75%	
M1-A	S ₁	486	1.070	H→L, 100%	564
	S ₂	302	0.038	H-2→L, 73%	
	S ₃	269	0.043	H-6→L, 59%	
M1-RA	S ₁	415	0.084	α H→L+4, 100%	
	S ₂	318	0.214	β H-2→L+1, 68%	
M1-R	S ₁	280	0.472	α H→L+3, 100%	
M1-C	S ₁	569	0.042	H-2→L, 100%	
	S ₂	339	0.639	H-4→L, 100%	
	S ₃	252	0.271	H-1→L+1, 62%	
M2	S ₁	296	0.521	H-4→L, 92%	$\approx$ 280
M2-A	S ₁	488	1.174	H→L, 100%	571
	S ₂	329	0.054	H→L+1, 91%	
	S ₃	240	0.145	H-2→L+1, 36% H-1→L+1, 29%	
M2-RA	S ₁	415	0.087	α H→L+4, 100%	
	S ₂	315	0.214	β H-2→L+1, 52%	
M2-R	S ₁	283	0.568	α H→L+4, 43% α H-1→L, 41%	
M2-C	S ₁	595	0.043	H-2→L, 99%	
	S ₂	340	0.724	H-4→L, 97%	
	S ₃	285	0.380	H→L+1, 95%	
M3	S ₁	295	0.378	H-4→L, 97%	$\approx$ 280
	S ₂	261	0.405	H→L+1, 93%	
M3-A	S ₁	487	1.120	H→L, 100%	576
	S ₂	321	0.032	H→L+3, 54%	
	S ₃	269	0.040	H-6→L, 57%	
M3-RA	S ₁	415	0.085	α H→L+4, 100%	
	S ₂	319	0.204	β H-2→L+1, 61%	
M3-R	S ₁	280	0.538	α H→L+3, 100%	
M3-C	S ₁	581	0.045	H-2→L, 99%	
	S ₂	339	0.669	H-4→L, 99%	
	S ₃	265	0.319	H→L+1, 76%	
M4	S ₁	280	0.521	H→L+1, 89%	$\approx$ 270
M4-A	S ₁	567	0.178	H→L, 100%	601
	S ₂	366	0.404	H→L+1, 86%	
	S ₃	263	0.452	H→L+6, 26%	
				H-5→L, 18%	
M4-RA	S ₁	416	0.058	α H→L+4, 100%	
	S ₂	317	0.204	β H→L+1, 16% β H→L, 14%	
M4-R	S ₁	279	0.799	α H-1→L, 40% β H→L+1, 40%	
M4-C	S ₁	466	0.024	H-3→L, 100%	
	S ₂	332	0.190	H-4→L, 66%	
	S ₂	287	0.564	H→L+1, 96%	

In the (**Mx-A**) enol tautomers spectra, it appears a new low-energy band whose wavelength depends on the substituents on the phenolic rings (486, 488, 487 and 567 nm for **M1-A**, **M2-A**, **M3-A** and **M4-A**, respectively). Actually, while the maximum absorption wavelength is found at very similar values for **M1-A**, **M2-A** and **M3-A**, having a nitro group in para position on the ring B and an hydrogen, a methoxy- or a methyl- as R1 substituent on ring A respectively, for **M4-A** it experiences a marked red shift instead (567 nm). So, the presence of a nitro group in ortho position on the ring B can explain the observed bathochromic effect of the Q band.

Looking at the nature of the bands, the λ_{max} of the ketone form is almost completely due to an electronic transition from inner occupied orbitals to the LUMO for **M1-M3** systems, while for **M4** result to be HOMO-LUMO in nature. The Q bands in the enol tautomers are originate by a HOMO→LUMO excitation in **M1A-M3-A** molecules but is HOMO-LUMO+1 for **M4-A**. Again, the structural (Table 1) and electronic (see Figure S2) changes due to the presence of NO₂ group in *ortho* position accounts for these differences.

Also the radical anion **Mx-RA** species displays red shifted bands compared to **Mx** spectra. For them, a new excited state appears at 415 nm (**M1-RA**, **M2-RA**, **M3-RA**) and 416 nm (**M4-RA**). In all cases, it results from a HOMO→LUMO+4 transition.

On the contrary, the neutral radical species **Mx-R**, display a unique absorption band in the same region of **Mx** species, around 280 nm, due to a HOMO→LUMO excitation.

Looking at the electronic spin density distribution for all the radical species **Mx-R** and **Mx-RA** (Figure S3), we note as in all cases the spin distribution is essentially concentrated on the ring B where the -NO₂ group are present.

The reduction process has been analyzed computing the reduction potentials reported in Table 3. Our data are in excellent agreement with the measured counterparts¹⁶ and they do not depend on the phenyl substitution pattern having almost the same values.

Table 3. Computed reduction potentials for studied compounds in acetonitrile solvent, employing B3LYP/6-31+G*. Experimental results are taken from ref. 16

Cmpd	$E_{\text{red}}^{\text{I/V}}$	
	calc	exp
M1	-1.05	-1.03
M2	-1.04	-1.02
M3	-1.07	-1.10
M4	-1.07	-1.06

Reaction Mechanism

Base-assisted process

The keto-enol tautomerization usually needs to be induced by a strong acid or base. In the experiment of Zhang et al,¹⁶ the potassium *tert*-butoxide anion was employed. In order to have information on the energetic of this process, we have determined the potential energy surface (PES) for this reaction using the same base as in the experiment. The obtained PES is reported in Figure 1 while the most significant geometrical parameters of the intermediates involved in the tautomerization reaction, are reported in Figure 2.

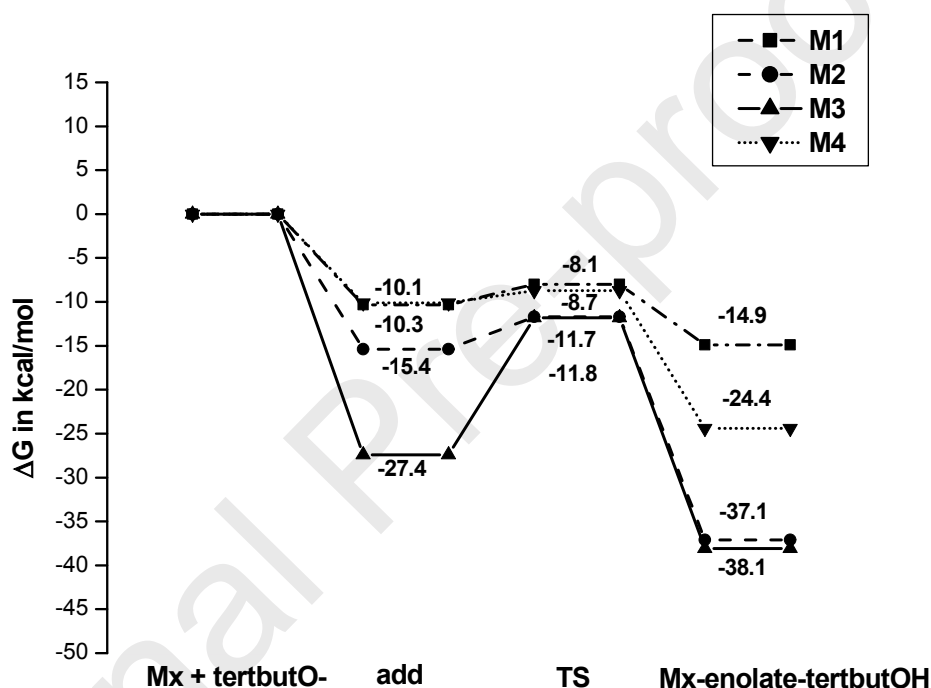


Figure 1. B3LYP/6-31+G* potential energy surface for the keto-enol tautomerization process in presence of tertbutO^- base in acetonitrile solution.

The energy profile clearly shows as the reaction is exoergonic and all the intercepted stationary points lie below the energies of the reagents. The reaction starts with the formation of an adduct between the two reactants (keto form + base) with a significant energy gain and in which the base molecule is oriented with his oxygen toward the methylene group of the methyl ketone (See Figure 2).

The greatest energetic stabilization of the adduct occurs for the **M2** (-15.4 kcal/mol) and **M3** (-27.4 kcal/mol) compounds. The subsequent proton extraction from the methylene group by the base through a transition state (TS), leads to the formation of the enol tautomer.

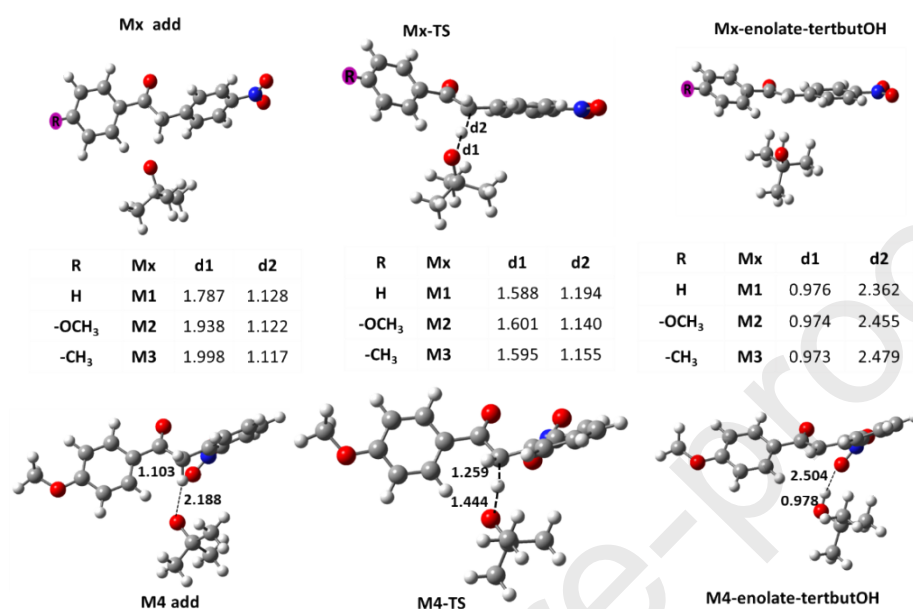


Figure 2. B3LYP/6-31+G* optimized geometries of transition states of **Mx** species related to the acid(**Mx**)-Base (*tert*-butoxide) reaction in acetonitrile ($\epsilon=35.69$). Distances are in Å.

The analysis of the vibrational mode of the transition state clearly indicates the H transfer from the $-\text{CH}_2$ -moiety of keto structure to the oxygen of *tert*-butoxide anion. Distances reported in Figure 2 show, indeed, the elongation of the C-H bond and the formation of the new O-H one. The energy barriers for the tautomerization process result feasible to be overcome, being the energy of the TS computed equal to -8.1 (**M1**), -11.7 (**M2**), -11.8 (**M3**) and -8.7 (**M4**) kcal/mol, and the reaction results to be exoergic with an energy gain that range from -14.9 (**M1**) to -38.1 (**M3**) kcal/mol. The higher energy barrier found for **M3** compound can be rationalized taking into account the significant electron-donor properties of the methoxy group present at the R1 position.

Electron and Proton transfer process

In the previously proposed mechanism,^{15,16} the authors hypothesized that the enol form could be reached also *via* an electroreduction path (see Scheme 2) according the following steps: **Mx** is reduced to the radical anion species **Mx-RA** that in turns can react with another **Mx** molecule producing, via a proton transfer, the enolate (**Mx-A**) and the radical **Mx-R** species. The cycle continues with the oxidation of **Mx-R** that, after a proton transfer toward the enolate **Mx-A**, restores

the starting neutral keto system. So, process includes a sequence of an electron and a proton transfer. Preliminary computations,¹⁶ previously performed on the transformation from **M1** to **M1-RA**, indicated that the reaction is exergonic (-6.4 kcal/mol), assuming the reliability of the proposed cycle on the basis of that finding.

Nevertheless, that value was obtained in gas-phase environment and does not take properly into account the solvent effects in the computed Gibbs energy values. For that reason, we have explored the same mechanism considering acetonitrile as solvent, in order to reproduce the experimental conditions.¹⁶ The H-transfer reaction has been thus explored determining and characterizing all the intermediates and the transition state involved in the **Mx** + **Mx-RA** → **Mx-R** + **Mx-A** reaction. The corresponding Gibbs free energy profile is reported in Figure 3, while the main geometrical parameters of the optimized structures for the adducts and transition states are given in Figure 4. Results show that for all the compounds, the reaction is endergonic by about 10 kcal/mol for **M1-M3** and by 18 kcal for **M4**. The barriers found range between 21.2 (**M1**) and 29.1 (**M4**) and are not low enough to allow the occurrence of the reaction at room temperature. The inspection of the TS's structures for this H-transfer reveals as the distances d_1 and d_2 , for all the four compounds, are very similar (about 1.2 and 1.4 Å, for d_1 and d_2 , respectively) meaning that the C-H bond is broken and the O-H one is prone for its formation (see Figure 4). The analysis of the negative vibrational frequencies confirm this behavior.

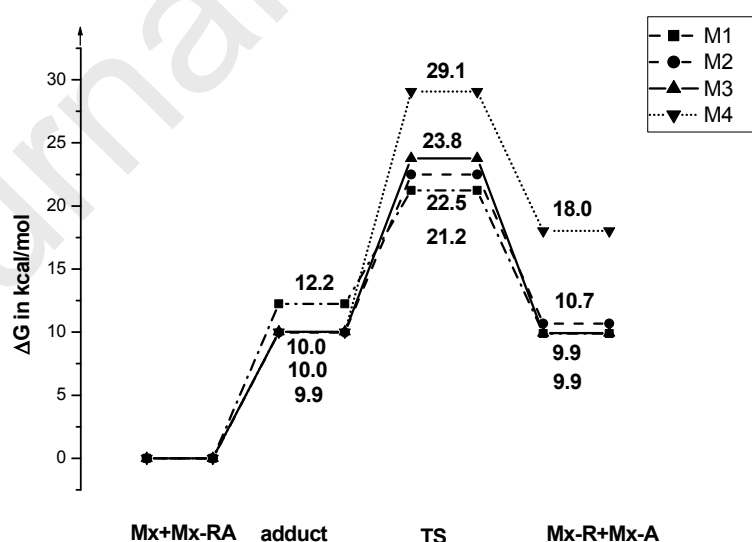


Figure 3. B3LYP/6-31+G* potential energy surface for the reaction between **Mx** and **Mx-RA** to obtain the enol **Mx-A** tautomer in acetonitrile environment.

Considering that this step of the mechanism occurs with positive reaction Gibbs energies and with fairly high barriers, we can predict that it is difficult to occurs.

The analysis of the thermodynamic data for the electron-transfer (ET) and proton-transfer (HT) processes, reported in Table 4, can give us additional information on the mechanism that occurs with less energy expenditure.

Table 4. B3LYP/6-31+G* free energy values (kcal/mol) related to the electrochromic mechanism depicted in Scheme 2.

Species	1st Step			2nd Step		
	ET	HT	Coupled	ET	HT	Coupled
M1	-47.0	9.9	-37.1	90.6	-53.5	37.1
M2	-46.4	10.7	-35.7	90.0	-54.3	35.7
M4	-46.8	9.9	-36.9	90.2	-53.3	36.9
M5	-46.3	18.0	-28.3	95.8	-67.5	28.3

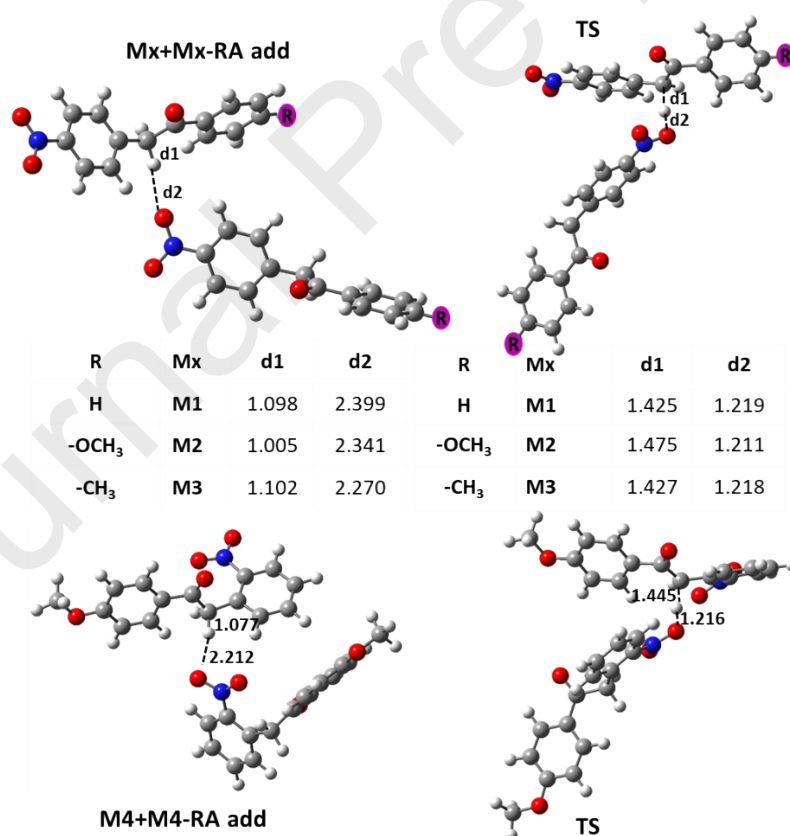


Figure 4. B3LYP/6-31+G* optimized geometries of intermediate and transition states species related to the H-transfer process in acetonitrile ($\epsilon=35.69$). Distances are in Å.

The first step (ET), triggered by the application of the electric field at a given voltage, is an exothermic process for all the examined compounds (e.g. -47.0 kcal/mol for **M1**). The subsequent proton transfer is endothermic instead (e.g. 9.9 kcal/mol for **M1**). In addition, as established building up the PES, it requires an activation energy ranging from 21.2 (**M1**) to 29.1 (**M4**) kcal/mol, suggesting that it is not a feasible process. Our data allow us to propose a new mechanism for the electrically generation of the enolate, that should occur through a proton coupled electron transfer (PCET in Scheme 2). That mechanism, which was already invoked in previous studies^{15,16}, was never quantified in terms of energy up to now. Actually, combining the energy of the two involved processes (ET and HT), it is now possible to provide the energy of PCET mechanism (Table 4). The occurrence of the PCET should be further hypothesized by considering the lack of absorption bands experimentally detected for radical and charged species (**Mx-RA**, **Mx-R** and **Mx-C**) in the spectroelectrochemical experiments.

Conclusions

Density functional theory has been used to elucidate the chemical and electrochemical behavior of induced reversible color switches of a series of methyl ketones systems.

The following conclusions can be outlined:

- the keto-enol tautomerization process assisted by a bases is an exergonic process with a low activation barrier;
- The tautomerization induced by an electrical stimulus can occurs throughout a reduction followed by a proton transfer or throughout a concerted proton coupled electron transfer. The former path it is critical in the proton transfer step which is thermodynamically unfavorable and requires activation barriers ranging from 21.2 to 29.1 kcal/mol depending on the compound examined. The concerted PCET appears to be favored since its exergonicity varies from -28.3 (**M4**) to -37.1 (**M1**);
- The computed excitation energies are in satisfactory agreement with the available experimental absorption wavelengths;
- The employed computational protocol is able to give oxidation potentials in excellent agreement with the experiment.

Acknowledgement

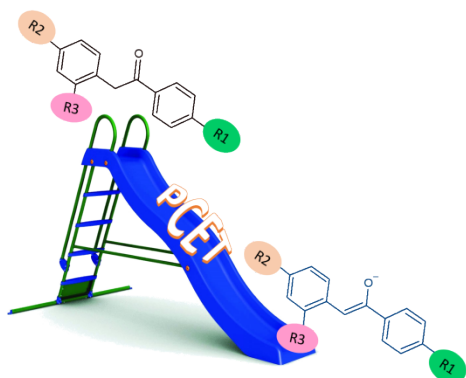
The authors thank the Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria for the support.

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TOC



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Manuscript Number: MOLLIQ-D-21-02001

All authors equally contributed to the various phases of the manuscript

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Conflicts of interest

There are no conflicts to declare