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1 Introduction

Silicon-based computers carry out mathematical operations using Boolean logic elements. The ability of molecules to process information similar to electronic systems was first demonstrated in 1993 by de Silva¹ and eventually this idea opened up a rapidly growing multidisciplinary research area.^{2,3} Molecular systems that exhibit sequential advanced logic functions such as those utilized for the construction of memory devices, delay and storage elements, and finite-state machines have great potential for applications^{3–7} and their design is a significant challenge in the field of molecular information technology.^{3–11}

In general, the molecular systems are designed according to the principles of modular PET (photo electron transfer)¹² in a 'fluorophore-spacer-receptor' or 'fluorophore-spacer-receptor1spacer-receptor2' format where the fluorophore and receptor sites are purposely separated.¹³ Namely, there is a fragment that is capable of serving as an "antenna" for the absorption of photons and of using the photon energy to transform the molecular structure, as well as a fragment whose reactivity changes as a result of the structural transformation. This is

Molecular logic gates based on benzo-18-crown-6 ether of styrylquinoline: a theoretical study[†]

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In the present work, we examine the possibility of a benzo-18-crown-6 ether of styrylquinoline molecule (1) in acetonitrile solvent to act as a sensor for the Ca⁺⁺ cation and as a molecular logical gate. DFT and TDDFT calculations are carried out using the M06-2X and the PBE0 functionals. The quinoline moiety is an electron donor and an H⁺ receptor, while the crown ether is a Ca⁺⁺ receptor forming host–guest complexes with Ca⁺⁺. The calculations show that there are 8 thermally stable forms, *i.e., trans* and *cis* isomers of neutral (1), protonated (1H⁺), complexed with Ca⁺⁺ (1Ca⁺⁺), and both protonated and Ca⁺⁺ complexed (1H⁺Ca⁺⁺), with different absorption and emission spectra, and which can be interconverted from one form to another. The addition of H⁺ and/or Ca⁺⁺ to 1 results in variation of the oscillator strength of the major absorption and emission peaks as well as in significant shifts of the major absorption and emission peaks are to UV and *vice versa*. Consequently, 1 is a candidate for a sensor for the Ca⁺⁺ cation. Furthermore it is shown that 1 can act as a molecular optical switch owing to its ability to be reversibly protonated and/or Ca⁺⁺ complexed with substantial accompanying differences in the spectral properties. Similarly, 1 can be used as a sensor molecular logic gate, in which using H⁺ and Ca⁺⁺ and irradiation as input, the emission output at 500, 470, 430, and 407 nm can be utilized as output to build AND, NOR, XOR, XNOR, INHIBIT, and IMPLICATION logic gates.

the principle of operation that is embodied in natural photosensitive systems. The absorption and emission properties of the designed molecules are modulated by different combinations of external input, such as light, metal ions, anions, solution pH, and solvent polarity.^{1–18} However, relatively few molecular systems are capable of performing multiple logic functions based on the modulation of both absorption and emission properties.^{19,20}

Diarylethylenes exist as two thermally stable isomer forms, the *trans* (*E*) and *cis* (*Z*) isomers. The isomers are transformed into each other under light illumination as a result of the reversible photoisomerization reaction. Owing to these properties, diarylethylenes are convenient models of photochromic molecular switches. Stilbene is the simplest diarylethylene.²¹ Stilbene is a prototypical molecule that undergoes a reversible *trans-cis* isomerization and exhibits photosensitive properties. Its photoisomerization has been extensively studied due to its important role in many areas of chemistry²² and photophysics²³ by both experimental²³⁻²⁹ and theoretical³⁰⁻³⁷ approaches, see ref. 36 and 37 and references therein. It has been generally accepted that the relaxation of both *cis* and *trans* isomers involves the central C—C bond twisting motion toward the perpendicular conformation.^{36,37}

In the case of styrylquinoline, photoisomerization and fluorescence are two competitive processes,²² see Scheme 1. After the absorbance of the *trans* (*E*) or *cis* (*Z*) molecule, the $E \rightarrow Z$ photoisomerization occurs generally by the well known diabatic

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Scheme 1 Absorption (dashed lines), photoisomerization (solid lines) and emission (dotted lines).

mechanism where there is a twist around the ethylenic bond towards an energy minimum at the perpendicular configuration (pc), at about 90°.³⁸ Thus, there exists a $S_1 \rightarrow S_0$ internal conversion (or $T_1 \rightarrow S_0$ intersystem crossing) followed by a relaxation to the ground state trans and cis isomers in roughly a 1:1 branching ratio, *i.e.*, ${}^{1,3}E^* \rightarrow {}^{1,3}pc^* \rightarrow {}^{1}pc \rightarrow \alpha^1 Z + (1 - \alpha)^1 E$, where the factor α is assumed to be ~0.5 in most cases. In some cases, specific structures may stabilize the S_1 state of the *E* geometry and increase the energy barrier to twisting³⁹ thus leading to fluorescence. Generally, the photoisomerization-fluorescence competition is affected by some factors, *i.e.*, the size and shape of molecules, the existence of heteroatoms, the temperature, the solvent etc.40-46 Fluorescence dominates in conditions such as low temperature,^{40,41} rigid media in dyes,⁴³ viscous solvents,⁴⁴ freezing the solutions to a rigid glass,⁴⁴ the presence of fitting ions in rings of adjacent groups,45 and strong intramolecular interactions in inert solvents.46

Styrylquinoline, like most of the diarylethylenes, isomerizes reversibly by the diabatic mechanism.³⁸ Budyka *et al.*⁴⁷ found that upon irradiating 2-styrylquinoline at 365 nm the photostationary state contains 64% of the *Z*-isomer, and further irradiation at 313 nm results in a new photostationary state with 33% of the *Z*-isomer. Thus, Budyka *et al.*⁴⁷ treated the first photostationary state with irradiation at 313 nm as "input 1" and protonation (treatment with HCl) as "input 2" with gaseous HCl or they treated the second photostationary state with irradiation at 365 nm as "input 1" and protonation as "input 2". On embedding 2-styrylquinoline in a polymer film, it can act as "AND", "OR", "NAND", "INHIBIT", "NOR" and "IMPLICATION" logic gates using absorbance as an output readout at 301, 342, 356, and 390 nm. It is also found that the photoexcitation of styrylquinoline results in changes in styrylquinoline basicity.⁴⁸

Crown ethers are good complex-forming compounds capable of selectively capturing cations into their cavities. This makes it possible to use crown ethers for separation of different-type cations and the stabilization of metal cations in organic media. The ability of crown ether to bind metal cations depends on the cavity size and the nature of heteroatoms.^{49,50} A combination of styrylquinoline and crown ethers would facilitate additional functions towards their function as molecular logic gates. It might be noted that sensors have been synthesized that have lumophores other than styrylquinoline, conjugated through a



Fig. 1 Photoinduced *trans-cis* isomerism in the presence of H⁺ and Ca⁺⁺ cations in acetonitrile solvent.

double bond to crown ethers.⁵¹ However, the combination of styrylquinoline with benzo-18-crown-6 ether has not been previously investigated, either theoretically or experimentally, to the best knowledge of the authors.

The field of study of molecular logical gates (MLGs) is a very interesting subject and currently its real applications using working models are limited. The present study aims to provide experimentalists with data regarding a potential MLG candidate. Here, we study the benzo-18-crown-6 ether of the styrylquinoline molecule, 1, see Fig. 1. The target of the present work is to examine the possibility of 1 being a Ca⁺⁺ sensor and/or a molecular logical gate (MLG), given that it meets the demands of both: quinoline is an electron donor and a proton acceptor, the crown ether is a Ca⁺⁺ receptor that can form host-guest complexes with the cation and, at the same time, the molecule exhibits photosensitive properties due to the presence of an ethylene fragment in the chromophore. The switching between trans and cis isomers can be controlled via irradiation and protonation of the quinoline nitrogen atom.47 As will be discussed below, the present results confirmed that 1 may perform as a molecular device. Due to reversibility between eight different forms any of these different photostationary states can be used as an initial state of MLG. It should be noted that application of fluorescence for the output readout has sometimes advantage over absorbance.52-57 Here, both absorbance and emission output have been used.

2 Computational details

The neutral and protonated forms of benzo-18-crown-6 ether of styrylquinoline and the neutral and protonated benzo-18crown-6 ether of styrylquinoline complexes with the Ca divalent cation were calculated using DFT calculations using the $M06-2X^{58,59}$ and $PBE0^{60}$ functionals in conjunction with the

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Table 1 Vertical excitation energies, ΔE (eV), λ_{max} (nm), and *f*-values for S₀ \rightarrow S₁ absorption and S₁ \rightarrow S₀ emission maxima, adiabatic excitation energies ΔE_{ad} (eV), and energy difference between *trans* and *cis* isomers, and ΔE_{tc} (eV) of the free stilbene and in acetonitrile solvent at the M06-2X or PBE0/6-31G(d,p) level of theory

		$S_0 \rightarrow S_1$				$S_1 \rightarrow S_0$			
		ΔE	λ_{\max}	<i>f</i> -value	$\Delta E_{ m ad}$	ΔE	λ_{\max}	<i>f</i> -value	$\Delta E_{ m tc}$
trans	M06-2X ^a	4.39	282.48	0.997	3.98	3.64	340.52	0.993	0.115
	$M06-2X^b$	4.27	290.30	1.121	3.62	3.18	390.13	1.299	0.149
	PBE0 ^c	4.02	308.41	1.108	3.66	3.29	376.77	1.143	0.230
	$PBE0^d$	3.97 $3.98,^{e} 4.22,^{e} 4.0^{f}$	311.96	1.124	$3.41 \\ 3.81,^g 3.85^h$	$3.07 \\ \sim 3.50^i \ 3.71^j$	404.39	1.335	$0.223 \\ 0.121^k$
cis	$\begin{array}{c} \text{M06-2X}^a\\ \text{M06-2X}^b\\ \text{PBE0}^c\\ \text{PBE0}^d \end{array}$	4.66 4.60 4.30 4.16 4.48 ^l	265.92 269.35 288.43 298.38	$0.385 \\ 0.462 \\ 0.413 \\ 0.482$	3.68 3.55 3.49 3.23 3.57 ^m	2.84 2.70 2.73 2.32 $\sim 2.85^n$	436.57 459.40 454.26 534.43	0.190 0.501 0.367 0.491	

^{*a*} Free stilbene. ^{*b*} In acetonitrile, ^{*c*} In acetonitrile, PBE0/6-31G(d,p)//M06-2X/6-31G(d,p). ^{*d*} In acetonitrile, PBE0/6-31G(d,p). ^{*e*} Expt, ref. 24. ^{*f*} Expt, ref. 26*a*. ^{*g*} In 3MP, ref. 26*c*. ^{*h*} In *n*-hexane, ref. 28*b*. ^{*i*} Expt, in *n*-hexane ref. 28*a*. ^{*j*} Expt, in *n*-hexane, ref. 28*b*. ^{*k*} Ab initio data in the gas phase, extrapolated at the CCSD(T)/cc-pV ∞ Z level of theory, ref. 35. ^{*l*} Expt, ref. 29. ^{*m*} From a fitting of the experimental spectrum, ref. 62. ^{*n*} Expt, in *n*-hexane, ref. 28*c*.

 $6-31G(d,p)^{61}$ basis set in the gas phase and in acetonitrile solvent. Both the *trans* and the *cis* isomers were fully optimized. The potential energy curves with respect to the torsion C—C angle which connected the two isomers for all four species were calculated. The absorption and the emission spectra of the studied structures were calculated *via* the TDDFT methodology.

The applicability of the methods employed here was tested by carrying out calculations on the absorption and emission spectra of stilbene (1,2-diphenylethylene) where experimental results exist, see Table 1. Our results are in good agreement with the experimental values^{24,26,28,29,62} and high level *ab initio* methods.³⁵ Thus, both M06-2X/6-31G(d,p) and PBE0/6-31G(d,p)//M06-2X/6-31G(d,p) methods are considered as a very good choice for the present study where the calculation of the absorption and emission spectra is crucial in order to characterize a molecular system as an appropriate one for the molecular logic gate. The spectra involving transitions to 30–40 singlet-spin excited electronic states of the calculated species were calculated both in the gas phase and in acetonitrile solvent.

Geometry optimization calculations in acetonitrile ($\varepsilon = 35.688$) solvent were carried out employing the polarizable continuum model (PCM).⁶³ This model is divided into a solute part lying inside a cavity, surrounded by the solvent part represented as a structureless material characterized by its macroscopic properties, *i.e.*, dielectric constants and solvent radius. This method reproduces solvent effects as well.⁶⁴

The protonation energy and the interaction energy of the Ca⁺⁺ cation with the crown ether were calculated and corrected with respect to the basis set superposition error (BSSE) *via* the counterpoise procedure.⁶⁵ All calculations were performed using the Gaussian 09 program package.⁶⁶ The coordinates of all the optimum structures are included in the accompanying ESI.[†]

3 Results and discussion

3.1 Geometry

The calculated structures of the lowest minima *trans* and *cis* isomers of neutral (1), protonated $(1H^+)$, complexed with Ca⁺⁺

(1Ca⁺⁺), and both protonated and Ca⁺⁺ complexed (1H⁺Ca⁺⁺) are shown in Fig. 2 and Fig. S1 of the ESI.[†] The lowest in energy *trans* or *cis* isomer is labeled as *trans*-**n** or *cis*-**n**, respectively, while the local minima isomers are labeled as *trans*-**n_b** or *cis*-**n_b**, *cis*-**n_c**, and *cis*-**n_d**. The various *trans* and *cis* isomers differ in the rotation of the C_3 - C_1 axis.

Selected geometries are given in Table 2 and Table S1 of the ESI,[†] while the Cartesian coordinates are given in Table S7 of the ESI,[†] Protonation of quinoline for both *cis* and *trans* forms and complexation of Ca to the crown ether in the *trans* form does not alter the geometry of the ethylene group of quinoline of **1** in the ground and excited states, *cf.* Table 2. In contrast, complexation of Ca⁺⁺ with the crown ether affects the dihedral angles about the double bond, *i.e.*, $\delta_{H1C1C2H2}$, $\delta_{C3C1C2C4}$, and $\delta_{NC3C1C2}$, in the lowest *cis* minimum in both the S₀ and S₁ states, while the subsequent protonation of quinoline reverses the effect.

In the calculated structures of the $1Ca^{++}$ and $1H^+Ca^{++}$ molecules, the O-Ca bond distance ranges from 2.516 to 2.745 Å, see Table S1 of the ESI.† The largest O-Ca values are observed in the S₁ minima. The Ca⁺⁺ cation is in the cavity of the crown ether, see Fig. S1 of the ESI.† The bond angles ϕ_{O1CaO4} and ϕ_{O3CaO6} range from 172 to 180 degrees and the ϕ_{O2CaO5} angles range from 156 to 161 degrees, for the lowest minima, see Table S1 of the ESI.† In the *cis*-1Ca⁺⁺ and *cis*-1Ca⁺⁺_b species a hydrogen van der Waals bond H···N is formed of about 2.1 Å between the N atom and the phenyl H atom, see Fig. 2 and Table 2 and Table S1 of the ESI.† Note that the intramolecular interactions are particularly strong in inert solvents making the torsional process practically forbidden⁴⁶ and the excited *cis*-1Ca⁺⁺ isomer decays by fluorescence.

The Mulliken charges of atoms are almost the same in the first excited (S₁) state as in the ground (S₀) state, see Table S2 of the ESI.[†] The N atom of quinoline has a charge of about $-0.6 e^-$ which is increased by $-0.1 e^-$ in the protonated molecules. Charge is transferred to the proton and it has $+0.4 e^-$. The O atoms of the uncomplexed crown ether have charges of about $-0.55 e^-$. The Ca⁺⁺ complexed species has a charge of $+1.53 e^-$,



Fig. 2 Calculated structures of the lowest minima of the 1, $1H^+$, $1Ca^{++}$, and $1H^+Ca^{++}$ trans and *cis* isomers in acetonitrile solvent at the M06-2X level of theory (H atoms = white, C = grey, O = red, N = blue and Ca = yellow spheres). Energy differences in eV are given.

thus, about half of the electron is shared with the O atoms and their charges are increased to $\sim -0.63 \ e^-$.

3.2 Energetics

The vertical excitation energies, ΔE_a for the $S_0 \rightarrow S_1$ absorption and ΔE_e for the $S_1 \rightarrow S_0$ emission maxima, and adiabatic excitation energies, ΔE_{ad} for the *trans* and *cis* isomers of the **1**, **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ molecules, as well as the energy difference between the isomers ΔE_{is} in the ground (S₀) and the first excited states (S₁) in acetonitrile solvent are collected in Table 3 and Tables S4, S5 of the ESI.[†]

The variation of the vertical excitation energies, $\Delta E_{\rm a}$ and $\Delta E_{\rm e}$, and adiabatic excitation energies, $\Delta E_{\rm ad}$, with respect to protonation and Ca⁺⁺ complexation of **1** is depicted in Fig. 3. The Ca⁺⁺ complexation leads to an increase of the $\Delta E_{\rm a}$, $\Delta E_{\rm e}$, and $\Delta E_{\rm ad}$ values for both *trans* and *cis* isomers, protonation

Table 2 Selected geometries, distances R in Å, angles ϕ and dihedral angles δ in degrees of the ground states S_0 (first line) and the first excited state S_1 (second line *in italics*) of the eight stable lowest energy structures

	R_{C1C2}	$\delta_{\rm H1C1C2H2}$	$\delta_{\rm C3C1C2C4}$	$\delta_{ m NC3C1C2}$	$\delta_{C1C2C3C5}$	$R_{\rm N-H}$	R _{O1-Ca}	R _{O2-Ca}	R _{O3-Ca}	R _{O4-Ca}	R _{O5-Ca}	R _{O6-Ca}	$\phi_{\rm O1CaO4}$	$\phi_{ m O2CaO5}$	$\phi_{ m O3CaO6}$	$R_{\mathrm{H}\cdots\mathrm{N}}$
trans-1	1.342	179.1	179.6	2.2	175.8											
	1.411	179.4	179.6	0.6	178.9											
cis-1	1.343	5.2	6.8	144.9	148.2											
	1.428	35.9	44.7	172.5	175.1											
trans-1H ⁺	1.351	179.3	179.9	178.3	178.3	1.017										
	1.399	179.8	179.7	179.7	179.7	1.013										
$cis-1H^+$	1.348	5.9	10.6	152.7	150.3	1.017										
	1.406	22.4	30.6	166.8	168.4	1.013										
trans-1Ca ⁺⁺	1.341	179.4	179.3	0.0	176.0		2.593	2.522	2.601	2.578	2.552	2.613	173.5	157.5	179.5	
	1.417	179.5	179.2	0.6	178.5		2.621	2.549	2.601	2.574	2.525	2.603	176.6	155.5	178.9	
cis-1Ca ⁺⁺	1.345	1.1	1.3	49.6	150.3		2.597	2.518	2.583	2.593	2.533	2.600	172.3	160.6	172.9	2.115
	1.422	10.2	15.4	11.3	174.1		2.609	2.527	2.588	2.588	2.545	2.619	172.8	160.6	173.4	2.040
trans-1H ⁺ Ca ⁺⁺	1.347	177.9	179.8	174.4	175.2	1.017	2.638	2.531	2.592	2.576	2.534	2.622	172.2	161.3	174.8	
	1.406	179.4	179.6	179.1	179.0	1.013	2.702	2.533	2.572	2.550	2.526	2.647	172.7	160.8	174.8	
cis-1H ⁺ Ca ⁺⁺	1.344	5.0	8.2	147.6	33.9	1.018	2.622	2.532	2.587	2.613	2.531	2.603	177.5	159.0	173.4	
	1.416	28.2	36.6	168.4	11.5	1.014	2.705	2.539	2.570	2.600	2.516	2.638	177.9	159.6	173.5	
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van der Waals distance between N and H atoms of the phenyl group, see Fig. 2.

Table 3 Vertical excitation energies, ΔE_a (eV), for $S_0 \rightarrow S_1$ absorption and ΔE_e (eV) for $S_1 \rightarrow S_0$ emission maxima, λ_{max} (nm), and *f*-values of absorption and emission, adiabatic excitation energies ΔE_{ad} (eV), energy difference ΔE_{is} (eV) between the isomers in the S_0 and S_1 states, and the energy gap for the conversion of the *trans* to *cis* molecule ΔE_{ts} (eV) of the **1**, **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ species in acetonitrile solvent at the M06-2X/6-31G(d,p) and PBE0/6-31G(d,p)//M06-2X/6-31G(d,p) (*in italics*) levels of theory

	$S_0 \rightarrow S_1$	L		$S_1 \rightarrow S_0$	$S_1 \rightarrow S_0$					
	ΔE_{a}	λ_{\max}	f	$\Delta E_{\rm e}$	λ_{\max}	f	ΔE_{ad}	$\Delta E_{\rm is}({ m S}_0)$	$\Delta E_{\rm is}({ m S_1})$	$\Delta E_{\rm ts}$
trans-1	3.58	346.38	1.3978	2.84	436.19	1.5315	3.21	0.00	0.00	1.66
	3.31	374.18	0.9915	2.84	436.46	1.3200	3.12	0.00	0.00	1.61
cis-1	3.98	311.87	0.9532	2.36	524.47	0.9693	3.24	0.19	0.22	
	3.54	350.58	0.4013	2.46	503.01	0.7945	3.19	0.29	0.36	
trans-1H ⁺	2.98	415.37	1.6309	2.55	486.79	1.8079	2.75	0.00	0.00	1.65
	2.79	444.99	1.0207	2.63	471.98	1.3633	2.76	0.00	0.00	1.69
$cis-1H^+$	3.04	407.23	0.7534	2.37	523.47	1.0829	2.69	0.20	0.14	
	2.60	477.13	0.2800	2.48	499.94	0.7170	2.70	0.29	0.23	
trans-1Ca ⁺⁺	3.83	324.10	1.8194	2.99	414.25	1.8765	3.40	0.00	0.00	1.73
	3.69	335.87	1.5651	3.05	406.90	1.7292	3.37	0.00	0.00	1.81
cis-1Ca ⁺⁺	4.18	296.65	0.6983	2.90	428.27	0.9909	3.41	0.18	0.19	
	3.81	325.07	0.3698	2.89	429.35	0.7377	3.24	0.26	0.13	
trans-1H ⁺ Ca ⁺⁺	3.26	379.86	1.6641	2.70	458.70	1.8228	2.97	0.00	0.00	1.70
	3.10	399.56	1.2435	2.81	441.59	1.6073	2.99	0.00	0.00	1.71
cis-1H ⁺ Ca ⁺⁺	3.38	366.92	0.7952	2.33	532.08	0.9177	2.88	0.20	0.11	
	3.02	409.90	0.4915	2.45	506.67	0.7995	2.88	0.28	0.17	

of **1** leads to a reduction of the values, while both complexation and protonation lead to a smaller increase of the values compared to $\mathbf{1Ca}^{++}$. Thus, the $\mathbf{1Ca}^{++}$ complex presents the largest ΔE_{a} , ΔE_{e} , and ΔE_{ad} values and $\mathbf{1H}^{+}$ has the lowest values (with the exception of ΔE_{e} for the *cis* isomer).

The dissociation energies DE of the calculated minima with respect to *trans*-1(or *cis*-1 for the *cis* isomers) + H⁺ (DE₁, *i.e.*, protonation energy), *trans*-1(*cis*-1) + Ca⁺⁺ (DE₂, *i.e.*, interaction energy of the Ca⁺⁺ cation with the crown ether), and *trans*-1(*cis*-1) + H⁺ + Ca⁺⁺ (DE₃) for the ground S₀ and the first excited states S₁ in acetonitrile solvent at the M06-2X/6-31G(d,p) level of theory with and without BSSE correction are given in Table 4 and Table S3 of the ESI.† We observe that the BSSE correction is less than 20% of the uncorrected value for the interaction energy of the Ca⁺⁺ cation with the crown ether, while for the protonation energy it is less than 0.5%. The protonation energy is 7.81 eV for the *trans*-1H⁺ isomer in the

 S_0 state and it is increased to 8.26 eV in the S_1 state. In the *trans*-**1H**⁺**Ca**⁺⁺ isomer the values are smaller by 0.13 eV than the values of *trans*-**1H**⁺. The interaction energy of the Ca⁺⁺ cation with the crown ether is 1.28 eV in the S_0 state and 1.09 eV in the S_1 state for the *trans*-**1Ca**⁺⁺ isomer. In the *trans*-**1H**⁺**Ca**⁺⁺ isomer the corresponding values are 1.15 and 0.93 eV, respectively. The total dissociation energies of *trans*-**1H**⁺**Ca**⁺⁺ with respect to *trans*-**1** + H⁺ + Ca⁺⁺ are 8.95 (S₀) and 9.30 eV (S₁). Similarly DE values as for the *trans* isomers are also calculated for the corresponding *cis* systems, *cf.* Table 4.

3.3 Absorption and emission spectra

The PBE0 and M06-2X absorption (in S_0 ; in the geometry of the ground state) and emission (in S_1 ; in the geometry of the first singlet excited state) spectra of the lowest in energy **1**, **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ *trans* and *cis* isomers in acetonitrile solvent are recorded and depicted in Fig. 4 and Fig. S2–S4 of the ESI.[†]



Fig. 3 Variation of the vertical excitation energies, ΔE_{a} for absorption and ΔE_{e} for emission, adiabatic excitation energies, ΔE_{ad} , and energy gap ΔE_{ts} for the switching between *trans* and *cis* isomers with respect to the protonation and the Ca⁺⁺ complexation of **1** in acetonitrile solvent at the M06-2X/6-31G(d,p) level of theory.

Table 4 BSSE corrected dissociation energies DE (eV) of the calculated minima with respect to *trans*-1(*cis*-1) + H⁺ (DE₁), *trans*-1(*cis*-1) + Ca⁺⁺ (DE₂), and *trans*-1(*cis*-1) + H⁺ + Ca⁺⁺ (DE₃) of the ground states S₀ and the first excited states S₁ in acetonitrile solvent at the M06-2X/6-31G(d,p) level of theory

	So			S ₁			
	DE1	DE_2	DE ₃	DE1	DE_2	DE ₃	
trans-1H ⁺	7.81			8.26			
$cis-1H^+$	7.79			8.34			
trans-1Ca ⁺⁺		1.28			1.09		
cis-1Ca ⁺⁺		1.29			1.11		
trans-1H ⁺ Ca ⁺⁺	7.68	1.15	8.95	8.11	0.93	9.19	
cis-1H ⁺ Ca ⁺⁺	7.66	1.15	8.94	8.19	0.96	9.30	

It should be noted that the calculated emission spectra display bands whose energies are higher than those of the S_1 to S_0 transition and which are experimentally invisible in most cases owing to Kasha–Vavilov's rule. These bands obtained from the TDDFT calculations indicate the location of higher-lying electronic states at the geometry of S_1 .

Both functionals predict similar absorption and emission spectra. In addition to the excitation energies, for $S_0 \rightarrow S_1$ absorption and emission, the corresponding values of λ_{max} (nm) and *f*-values for absorption and emission are also given in Table 3 and Tables S4 and S5 of the ESI† in acetonitrile solvent and in Table S6 of the ESI† in the gas phase. It may be noted that the PBE0 functional predicts generally larger λ_{max} for absorption and smaller λ_{max} for emission compared to M06-2X and larger *f*-values than M06-2X in all cases.

A comparison between the spectra in the gas phase and in acetonitrile solvent shows generally a shift to lower energies in the presence of solvent. The largest shift for absorption λ_{\max} is calculated for *trans*-**1H**⁺**Ca**⁺⁺ at 61 nm, while for emission, the largest shift is found for λ_{\max} of *cis*-**1H**⁺**Ca**⁺⁺ at 129 nm. The main peaks of the absorption and emission spectra of the solvent acetonitrile itself is calculated at 110 and 133 nm,

respectively, and do not influence the main peaks of the studied molecules. In what follows, the results of the calculations including the solvent will be discussed.

The major excitation peak in the absorption and emission spectra corresponds to HOMO \rightarrow LUMO (H \rightarrow L) excitation for all 1, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ for both *trans* and *cis* isomers, while it corresponds to $H-1 \rightarrow L$ excitation for $1H^+$. For 1, the major absorption peak is calculated in UV, at 346(374) nm and 312(351) nm for the trans and cis isomer, while the major emission peak is calculated in vis, at 436(436) nm and 524(503) nm, respectively at the M06-2X(PBE0) level of theory, see Table 3. Protonation results in red shifts of the major peaks with the exception of the emission peak of *cis*-1H⁺. All peaks are in the vis spectra, *i.e.*, major absorption peaks: 415(445) and 407(477) nm, major emission peaks: 487(472) and 523(500) nm for the trans-1H⁺ and cis-1H⁺ isomers, respectively. In contrast, complexation of Ca⁺⁺ with the crown ether of **1** results in blue shifts of both major absorption and emission peaks of 1, i.e., absorption peaks: 324(336) and 297(325) nm and emission peaks: 414(407) and 428(429) nm for the trans-1Ca⁺⁺ and cis-1Ca⁺⁺ isomers, respectively. Finally, both protonation and Ca⁺⁺ complexation result in red shifts of all major absorption and emission peaks of 1, and the values are 380(400) and 367(410) nm [absorption peaks in UV] and 459(442) and 532(506) nm [emission peaks] for the trans-1H⁺Ca⁺⁺ and *cis*-1H⁺Ca⁺⁺ isomers, respectively, see Table 3.

The oscillator strengths of the major peaks are large. The trans isomers present larger oscillator strengths than cis isomers for all four 1, 1H⁺, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ species for both major absorption and emission peaks. The oscillator strength of the trans-1 isomer is 1.40[1.53](0.99[1.32]) for the absorption[emission] major peak using M06-2X(PBE0) and it increased with the addition of H⁺ and/or Ca⁺⁺. The largest value is observed for the 1Ca⁺⁺ complex at 1.82[1.88](1.57[1.72]). The smallest oscillator strengths are observed for the cis-1H⁺ and cis-1Ca⁺⁺ species, see Table 3. With respect to the change in the fvalues with the addition of H⁺ and/or Ca⁺⁺, both functionals predict the same trends. Addition of H⁺ and/or Ca⁺⁺ increases the oscillator strength of the major absorption and emission peaks of the *trans* isomer. For the *cis* isomer, the addition of H⁺ or Ca⁺⁺ decreases the oscillator strength of the major absorption, while the addition of both H⁺ and Ca⁺⁺ does not affect the *f*-value. Finally, the addition of H⁺ and/or Ca⁺⁺ does not affect significantly the oscillator strength of the major emission peak of the *cis* isomer, see Table 3. Thus, the addition of H^+ and/or Ca⁺⁺ results in variation of the oscillator strength of the major absorption and emission peaks and mainly it results in shifts of the major absorption and emission peaks in the vis spectral area and mainly from UV to vis and back to UV. Consequently, 1 is a candidate for a sensor for the Ca⁺⁺ cation and as a molecular optical switch owing to its ability to be reversibly transformed and the substantial difference in the spectral and complex-forming properties of both trans and cis dye isomers.

3.4 Molecular orbitals

The electron density plots of the HOMO (H), HOMO-1 (H-1) and LUMO (L) involved in the s_1 or s_2 excitation of the



Fig. 4 Absorption (under S_0) and emission (under S_1) spectra of the lowest in energy **1**, **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ trans and cis isomers in acetonitrile solvent at the PBE0 level of theory.

absorption (S_0) and emission (S_1) spectra of the 1, 1H⁺, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ molecules are depicted in Fig. 5 and 6. The relative energies of MOs are given in parentheses. For all species the H-1, H, and L are the same in the S_0 and S_1 states with the exception of the *cis*-1H⁺Ca⁺⁺ complex, where the H-1 and H are interchanged. The energy difference $H \rightarrow L$ is larger in the absorption (S_0) spectrum than that in the emission (S_1) spectrum for all species, while the energy difference between H-1 and H is smaller in the absorption (S₀) spectrum than that in the emission (S₁) spectrum with the exception of the $1H^+$ species. The energy difference between H-1 and H in the absorption ranges from 0.02 (*cis*- $1H^+Ca^{++}$) to 0.81 (*trans*- $1Ca^{++}$) eV and in the emission ranges from 0.08 (*trans*- $1H^+$) to 1.19 (*trans*- $1Ca^{++}$) eV. In $1H^+$ (both S₀ and S₁), *cis*-1 (S₀ only), and $1H^+Ca^{++}$ (S₀ only) the H and H-1 are energetically degenerate with an energy difference of up to 0.2 eV.



Fig. 5 Electron density plots of the HOMO (H), HOMO-1 (H-1) and LUMO (L) involved in the s_1 or s_2 excitations of the absorption (S₀) and emission (S₁) spectra of **1** and **1H⁺** molecules. The relative energies of MOs are given in parentheses; *f*-values and λ_{max} in nm of the s_1 or s_2 excitations are also given.

The electron densities of H and H-1 are located on styrylquinoline and benzo-crown ether, respectively, with the exception of the $1H^+$ cation (for both S_0 and S_1 and both *trans* and *cis* isomers) and the *cis*- $1H^+Ca^{++}$ species (for S_0), where the



Fig. 6 Electron density plots of the HOMO (H), HOMO-1 (H–1) and LUMO (L) involved in the s_1 or s_2 excitations of the absorption (S_0) and emission (S_1) spectra of the **1Ca⁺⁺** and **1H⁺Ca⁺⁺** molecules. The relative energies of MOs are given in parentheses; *f*-values and λ_{max} in nm of the s_1 or s_2 excitations are also given.

electron densities of H and H–1 are interchanged. In all cases, the electron density of the L is detected in styrylquinoline. The s_1 excitation corresponds to charge transfer from crown ether to styrylquinoline in *trans*-1H⁺ (both absorption and emission spectra), in *cis*-1H⁺ (for S_1), and in *cis*-1H⁺Ca⁺⁺ species (for S_0). In all other cases the s_2 excitation corresponds to charge transfer.

The charge transfer excitation in 1, $1Ca^{++}$, and $1H^+Ca^{++}$ has significant smaller oscillator strength than the other excitations, however in $1H^+$ even though the oscillator strength of the charge transfer excitation is smaller than the other one, it is not negligible and it is about 100 times larger than the corresponding values of 1, $1Ca^{++}$, and $1H^+Ca^{++}$ species, see Fig. 5 and 6.

3.5 Logic gates

With appropriate selection of the irradiation wavelength, molecule **1** could be enriched with the *trans* or *cis* isomer. The photoisomerization input of 746(770) nm corresponds to the energy gap for the isomerization of **1** from *trans* to *cis* and 843(939) nm from *cis* to *trans* at the M06-2X(PBE0) level of theory, see Table 3. When irradiation is used as a second input for the **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ species the output changes accordingly, see Table 3.

The truth tables resulting from **1** using two ionic input, namely, H^+ and Ca^{++} and photoisomerization input and absorption modes as output in the UV/visible area at 336, 351, 374, 400 and 445 nm are given in Table 5. The PBE0 λ_{max} and their oscillator strength are provided in Table 5 for convenience as well as the oscillator strength at the absorption output. A threshold *f*-value can be used for the discrimination between the "on" states, *i.e.*, output = 1 and "off" states.^{4,14} Here, a threshold *f*-value of 0.4 is used, see Table 5 and Fig. 4. Thus, from the truth tables of Table 6, we observe that 1, using two ionic and photoisomerization input, can be used as a molecular logic gate for AND, NOR, NOT, and INHIBIT logic operations at the five selected λ absorption output values of 336, 351, 374, 400 and 445 nm, see Table 6.

Budyka *et al.*⁴⁷ embedded 2-styrylquinoline in a polymer film and they found that using absorbance as an output readout and irradiation (for the conversion of *trans* to *cis* isomer and *vice versa*) and protonation as input, it can act as "INHIBIT" and "NOR" logic gates at 342 nm, "OR" and "IMPLICATION" logic gates at 356 nm and an "AND" logic gate. In the present study, for the benzo-18-crown-6 ether of styrylquinoline using absorbance as an output readout and irradiation (for the conversion of *trans* to *cis* isomer and *vice versa*) and protonation as input, it can act as "INHIBIT" at 351 nm. Thus, the addition of the crown ether on 2-styrylquinoline changes significantly the utility of 2-styrylquinoline.

The truth tables resulting from 1 enriched in the trans isomer using two ionic input, namely, H⁺ and Ca⁺⁺ and photoisomerization input and emission modes as output in the visible area at 500, 470, 430, and 407 nm are given in Table 7. As mentioned in the Introduction, there is a photoisomerization-fluorescence competition which is affected by some factors such as temperature, viscous solvents, use of rigid media in dyes, etc.; for instance, freezing the solution makes fluorescence the primary process. The PBE0 λ_{max} and their oscillator strength are provided in Table 7 for convenience as well as the oscillator strength at the emission output. It should be noted that the same truth tables result using both the M06-2X and PBE0 emission spectra. A threshold f-value of 0.5 is used for the discrimination between the "on" states, i.e., output = 1 and "off" states, *i.e.*, output = 0, see Table 7 and Fig. 4. Thus, from the truth tables of Table 7, we observe that 1, using two ionic and photoisomerization input, can be used as a molecular logic gate for AND, NOR, XOR, XNOR, INHIBIT, and IMPLICATION logic operations at the four selected λ output values of 500, 470, 430, and 407 nm, see Table 8.

Finally, it might be noted that it is possible for **1** to be used as a MLG embedded in a polymer film as 2-styrylquinoline is used.⁴⁷

3.6 Transition states

The calculated structures of the transition state (ts-) for the isomerization of the *trans* to *cis* isomer of the $1, 1H^+, 1Ca^{++}$, and $1H^+Ca^{++}$ *trans* and *cis* isomers are shown in Fig. 7. With the

 Table 5
 Truth tables resulting from 1 using two ionic input and photoisomerization (irradiation) input and absorption mode as output (the oscillator strength is provided)

Input1: (irradiation by light) ^a	Input2: (H ⁺)	Input3: (Ca ⁺⁺)	λ_{\max} (nm) (<i>f</i> -value)	Output1: (336 nm)	Output2: (351 nm)	Output3: (374 nm)	Output4: (400 nm)	Output4: (445 nm)
0	0	0	374 (0.99)	0	0	1	0	0
1	0	0	351 (0.40)	0	1	0	0	0
0	1	0	445 (1.02)	0	0(0.29)	0	0	1
1	1	0	477 (0.28)	0	0	0	0	0
0	0	1	336 (1.56)	1	0 (0.30)	0	0	0
1	0	1	325 (0.37)	0	0	0	0	0
0	1	1	400 (1.24)	0	0	0	1	0
1	1	1	410 (0.49)́	0	0	0	1(0.40)	0

^a 770 nm results in enrichment of the *cis* isomer of **1** and 939 nm results in enrichment of the *trans* isomer.

 Table 6
 Molecular logic operation for 1 starting from 1 enriched in the trans isomer using two ionic input and photoisomerization input and absorption modes as output

Conditions	Output1: 336 nm	Output2: 351 nm	Output3: 374 nm	Output4: 400 nm	Output4: 445 nm
Irradiation ^{a} + H ⁺ in the absence of Ca ⁺⁺	_	INHIBIT ^b	NOR	_	INHIBIT ^c
Irradiation ^{a} + H ⁺ in the presence of Ca ⁺⁺	NOR	_	_	NOT^d	_
$H^+ + Ca^{++}$ (no irradiation ^{<i>a</i>})	$INHIBIT^{b}$	_	NOR	AND	INHIBIT ^c
$H^{+} + Ca^{++}$ (after irradiation ^{<i>a</i>})	_	NOT ^e	_	AND	_
Irradiation ^{a} + Ca ⁺⁺ in the absence of H ⁺	$INHIBIT^{f}$	INHIBIT^g	NOR	_	_
Irradiation ^{a} + Ca ⁺⁺ in the presence of H ⁺	_	—	—	NOT^d	NOR

^{*a*} Depending on the initial structure of the MLG, *i.e.*, 770 (for *trans*-1), 734 (*trans*-1H⁺), and 685 nm (*trans*-1Ca⁺⁺). ^{*b*} The second input is H⁺. ^{*c*} The first input is H⁺. ^{*d*} For irradiation. ^{*e*} For both. ^{*f*} The first input is Ca⁺⁺. ^{*g*} The second input is Ca⁺⁺.

 Table 7
 Truth tables resulting from 1 using two ionic input and photoisomerization input and emission modes as output (the oscillator strength is provided)

Input1: (irradiation by light) ^a	Input2: (H^+)	Input3: (Ca ⁺⁺)	$\lambda_{\max} (nm) $ (<i>f</i> -value)	Output1: 500 nm	Output2: 470 nm	Output3: 430 nm	Output4: 407 nm
0	0	0	436 (1.32)	0	0	1	0
1	0	0	503 (0.79)	1(0.74)	0	0	0
0	1	0	472 (1.36)	0 (0.30)	1	0	0
1	1	0	500 (0.72)	1 (0.72)	0 (low, 0.14)	0	0
0	0	1	407 (1.73)	0	0	0	1
1	0	1	429 (0.74)	0	0	1 (high, 0.74)	0 (low, 0.16)
0	1	1	441 (1.61)	0	0 (low, 0.30)	1 (high, 1.30)	0 ,
1	1	1	507 (0.80)	1(0.70)	0 (low, 0.10)	0	0

 Table 8
 Molecular logic operation for 1 starting from 1 enriched in the trans isomer using two ionic input and photoisomerization input and emission modes as output

Conditions	Output1: 500 nm	Output2: 470 nm	Output3: 430 nm	Output4: 407 nm
Irradiation ^{<i>a</i>} + H ⁺ in the absence of Ca ⁺⁺ Irradiation ^{<i>a</i>} + H ⁺ in the presence of Ca ⁺⁺ H ⁺ + Ca ⁺⁺ (no irradiation ^{<i>a</i>})	AND	INHIBIT ^b — INHIBIT ^b	NOR XOR XNOR	 NOR INHIBIT [⊄]
H + Ca (after irradiation) Irradiation ^{<i>a</i>} + Ca ⁺⁺ in the absence of H ⁺ Irradiation ^{<i>a</i>} + Ca ⁺⁺ in the presence of H ⁺	IMPLICATION [*] INHIBIT ^e —	 NOR	INHIBIT ^c INHIBIT ^c	— INHIBIT ^c —

^{*a*} Depending on the initial structure of the MLG, *i.e.*, 770 (for *trans*-1), 734 (*trans*-1H⁺), and 685 nm (*trans*-1Ca⁺⁺). ^{*b*} The first input is H⁺. ^{*c*} The first input is Ca⁺⁺. ^{*d*} IMPLICATION with first input Ca⁺⁺. ^{*e*} The first input is irradiation.



Fig. 7 Calculated structures of the ts-1, ts-1H⁺, ts-1Ca⁺⁺, and ts-1H⁺Ca⁺⁺ transition states in acetonitrile solvent in the S₀ state and pc minimum in the S₁ state (see Scheme 1). (H atoms = white, C = grey, O = red, N = blue and Ca = yellow spheres).

exception of $1Ca^{++}$, there are some small differences in geometry of the calculated transition states in the S₀ state and pc minimum in the S₁ state (see Scheme 1). This is reasonable because the potential surface around the pc minimum in the S₁ state is floppy and there is a conical intersection between the S₀ and S₁ states. The HCCH dihedral angle (or torsion C=C angle) δ (degrees) is about 90 degrees, see Table 9.

The potential energy curves for the isomerization with respect to the reaction coordinate (HCCH dihedral angle or torsion C=C angle) in acetonitrile solvent is shown in Fig. 8. The energy gaps $\Delta E_{\rm ts}$ of the four molecules are similar and they range from 1.65 to 1.73 eV at the M06-2X/6-31G(d,p) level of theory, see Table 3. The largest value is observed for the **1Ca**⁺⁺ species for both M06-2X and PBE0 functionals. The same trend as for the $\Delta E_{\rm a}$, $\Delta E_{\rm e}$, and $\Delta E_{\rm ad}$ values is observed, either the Ca⁺⁺ complexation is followed by the protonation or the protonation

Table 9 Vertical excitation energies between two electronic states S_0 and S_1 , ΔE_a (eV, in the transition state) and ΔE_e (eV, in the pc minimum of S_1), the HCCH dihedral angle (or torsion C=C angle) δ (degrees) and adiabatic excitation energies ΔE_{ad} (eV) of the transition state ts-**1**, ts-**1H**⁺, ts-**1Ca**⁺⁺, and ts-**1H**⁺Ca⁺⁺ in acetonitrile solvent at the M06-2X/6-31G(d,p) and PBE0/6-31G(d,p)//M06-2X/6-31G(d,p) (*in italics*) levels of theory

	$S_0 \rightarrow S_1$		$S_1 \rightarrow S_0$				
	ΔE_{a}	δ	$\Delta E_{ m e}$	δ	ΔE_{ad}		
ts-1 ts-1H ⁺ ts-1Ca ⁺⁺ ts-1H ⁺ Ca ⁺⁺	2.87 (2.68) 1.55 (0.60) 2.85 (2.73) 2.51 (2.43)	87.5 86.6 90.2 91.5	0.16 (0.37) 0.19 (0.01) 1.10 (1.04) 0.07 (0.11)	83.0 86.6 90.2 93.6	1.50 (1.54) 0.56 (0.33) 1.93 (1.87) 0.77 (0.86)		



Fig. 8 Potential energy curve for isomerization with respect to the reaction coordinate (HCCH dihedral angle or torsion C=C angle) in acetonitrile solvent at the M06-2X level of theory.

first occurs followed by the Ca⁺⁺ complexation (with the exception of ΔE_e for the *cis* isomer), see Fig. 3.

The vertical excitation energies between two electronic states in the transition state of S₀ and the pc minimum of the S₁ state, and adiabatic excitation energies of ts-1, ts-1H⁺, ts-1Ca⁺⁺, and ts-1H⁺Ca⁺⁺ in acetonitrile solvent at the M06-2X/6-31G(d,p) and PBE0/6-31G(d,p)//M06-2X/6-31G(d,p) (*in italics*) levels of theory are given in Table 9. The smallest values are calculated for ts-1H⁺, with 0.33 eV for the ΔE_{ad} energy, while the largest values are observed for ts-1Ca⁺⁺ with 1.87 eV for the ΔE_{ad} energy. For stilbene the corresponding value at SA-CAS/6-31G was calculated at 1.92 eV,⁶⁷ very close to our value for 1.

The absorption spectra of the ts-1 ts-1H⁺, ts-1Ca⁺⁺ and ts-1H⁺Ca⁺⁺ structures and spectra of the pc minimum of the S₁ state in acetonitrile solvent at the PBE0 level of theory are depicted in Fig. S5 of the ESI.[†] The *f*-values and λ_{max} in nm of the s₁ or s₂ excitations are given in Fig. S6 of the ESI.[†] For the four molecules, the first s₁ excitation in the absorption spectra is red-shifted compared to s₁ excitation of both *trans* and *cis* isomers, see Table 3 and Fig. S6 of the ESI.[†]

Electron density plots of H, H–1, and L involved in the s₁ or s_2 excitation of the absorption (S_0) spectrum of ts-1 ts-1H⁺, ts-1Ca⁺⁺ and ts-1H⁺Ca⁺⁺ structures and that of the spectrum of pc minimum of the S_1 electronic state of 1, 1H⁺, 1Ca⁺⁺, and $1H^+Ca^{++}$ are shown in Fig. S6 of the ESI.[†] The relative energies of the MOs are given in parentheses. The s₂ excitation corresponds to charge transfer from crown ether to styrylquinoline, with the exception of ts-1Ca⁺⁺ where the charge transfer excitation is the s₅ excitation. The oscillator strengths of charge transfer excitation are very small. The s₁ excitation of the pc spectrum of S_1 of 1, 1H⁺, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ corresponds to a $H \rightarrow L$ excitation with a large coefficient and to a $H \leftarrow L$ with a small coefficient which is an indication that the minimum is on conical intersection. Comparing the MOs in trans and cis isomers with the transition states, we observe that there are differences between the H, H-1, and L of trans and the transition state in the case of 1H⁺, while for the remaining three species, 1, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ they are similar. The MO relative energy differences in $H-1 \rightarrow H$ are large, while the $H \rightarrow L$ is smaller in the transition states than those values of *trans* and *cis* isomers, compare Fig. 5 and 6 with Fig. S6 of the ESI.[†]

4 Summary and conclusions

In the present work, we study the benzo-18-crown-6 ether of styrylquinoline molecule (1) in acetonitrile *via* DFT and TDDFT calculations using the M06-2X and the PBE0 functionals. Quinoline is an electron donor and an H⁺ receptor. The crown ether is a Ca⁺⁺ receptor forming host–guest complexes with the cation. There are 8 thermally stable forms, *i.e.*, *trans* and *cis* isomers of neutral (1), protonated (1H⁺), complexed with Ca⁺⁺ (1Ca⁺⁺), and both protonated and Ca⁺⁺ complexed (1H⁺Ca⁺⁺), which have different properties (absorption and emission spectra) and which can be converted from one to the other by protonation/deprotonation and/or Ca⁺⁺ complexation/decomplexation. Their geometries, energetics, chemical bonding, and absorption and emission spectra were calculated.

Both PBE0 and M06-2X predict similar absorption and emission spectra for all studied species. Ca^{++} complexation leads to an increase of the vertical excitation energies of absorption (ΔE_a), emission (ΔE_e), and adiabatic excitation energies (ΔE_{ad}) for both *trans* and *cis* isomers resulting in blue shifts of both major absorption and emission peaks of **1**. Protonation of **1** leads to a reduction of the ΔE values, corresponding to red-shifts of the major peaks which are all found in the region of vis spectra. Both complexation and protonation lead to a reduction of the ΔE values to smaller values than the corresponding values of **1**, *i.e.*, red shifts of all major absorption and emission peaks of **1**.

The *trans* isomers present larger oscillator strengths than *cis* isomers for all four **1**, **1H**⁺, **1Ca**⁺⁺, and **1H**⁺**Ca**⁺⁺ species for both major absorption and emission peaks. The addition of H⁺ and/or Ca⁺⁺ results in variation of the oscillator strength of the major absorption and emission peaks and in shifting of the major absorption and emission peaks in the vis spectral area and mainly from UV to vis and back to UV. Consequently, **1** is a candidate for a sensor for the Ca⁺⁺ cation and as a molecular optical switch owing to its ability to be reversibly transformed and the substantial difference in the spectral and complexforming properties of both *trans* and *cis* dye isomers.

The s_1 ($H \rightarrow L$) excitation corresponds to the charge transfer from crown ether to styrylquinoline in *trans*-1H⁺ (both absorption (S_0) and emission spectra (S_1)), *cis*-1H⁺ (for S_1), and *cis*-1H⁺Ca⁺⁺ species (for S_0); in all other cases the s_2 ($H-1 \rightarrow L$) excitation corresponds to the charge transfer from crown ether to styrylquinoline. The charge transfer excitation in 1, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ has significantly smaller oscillator strength than the other excitation, however in 1H⁺ even though the oscillator strength is still smaller than the other one, it is not negligible and is about 100 times larger than the corresponding values of those of 1, 1Ca⁺⁺, and 1H⁺Ca⁺⁺ species.

We found that 1 can be used as a sensor molecular logic gate. Using $H^{\scriptscriptstyle +}$ and $Ca^{\scriptscriptstyle ++}$ and irradiation as input, the

absorption output at 336, 351, 374, 400 and 445 nm can be utilized as output to build AND, NOR, NOT, and INHIBIT logic operations, while the emission output at 500, 470, 430, and 407 nm can be utilized as output to build AND, NOR, XOR, XNOR, INHIBIT, and IMPLICATION logic gates.

It should be noted that it is possible for 1 to be used as a MLG embedded in a polymer film as the 2-styrylquinoline is used. Given that the field of study of MLG is a very interesting topic and currently its real applications using working models are limited, the present paper can provide the experimentalists with data to develop a working device using the proposed system as a MLG.

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