A computational study of a light-driven artificial device: a third generation rotational photo-molecular motor in dilute solutions

Costantino Zazza, Stefano Borocci and Nico Sanna

A third-generation artificial photo-molecular motor, featuring two photo-switchable rotating moieties in connection with a pseudoasymmetric molecular centre, is investigated by combining quantum-mechanics (QM) algorithms with classical molecular dynamics (MD) propagators. In particular, in the present contribution we have addressed such a molecular motor in different rotational isomers following the experimental observations arising from the application of multiple spectroscopic techniques in dilute solutions. At first, we focused our attention on the reproduction of the UV/Vis absorption spectrum in two solvents (acetonitrile and cyclohexane) with different gradient-corrected density functional theory (B3LYP, Cam-B3LYP, PBE, PBE0) functionals in conjunction with the conductor-like and polarizable continuum model (C-PCM). Furthermore, we refined the absorption signals by combining a classical MD sampling at room-temperature with DFT-based electronic degrees of freedom to compute perturbed excitation wavelengths driven by thermal fluctuation and solvation effects. In this respect, we have modelled the investigated artificial motor within solution nanodroplets with solvent molecules treated contextually at atomistic level and via a dielectric and polarizable continuum model.

Introduction

The design and construction of machines and devices at molecular sizes is a stimulating scientific challenge and a primary objective for future-oriented nano-technologically advanced smart materials. In this respect, either natural or synthetic molecular machines and devices of increasing complexity and functionalities have emerged in literature with the basic capabilities of converting chemical energy into mechanical forces responsible for conformational changes. Moreover, single-molecule machines appear to be ideal candidates in this research field because they allow high densities while conserving conformational flexibility which may open up the route toward novel intrinsic functionalities at nanoscale level. The general trend is basically that of classifying molecular machines and devices in different domains: (i) brownian nanoscale devices in which thermal fluctuations under non-equilibrium conditions can activate conformational changes comparable to the switching mechanism occurring at the nanoscale level; (ii) stimuli-responsive molecular systems where quasi 1-D conformational changes are essentially driven by external perturbations like for example chemical reactions, pH-variations, electrochemical oxidation/reduction and UV/Vis radiative exposure. More precisely, a molecular machine is a particular type of device in which the molecular subunits can change their relative positions as a result of some external perturbation/stimulus. In this context, inspired by living organisms, directionally controlled molecular switching mechanisms in single-molecule systems and/or supramolecular aggregates of increasing complexity have been proposed and characterized in the last 3 decades by chemical engineers. Importantly, the contributions in this field have been enriched by theoretical and computational investigations which actually provide accurate information at the atomistic level – sometimes even difficult to access via routine experiments – in the presence of large and flexible complex molecular systems. Always remaining in the context of the QM/MM schemes, we previously studied from a computational point of view both electrochemically and light driven molecular systems in dilute solution as proposed by D. Leigh and F. Stoddart, A. Credi and B. Feringa.

In the present contribution, we propose a simulation environment essentially based on quantum-mechanics (QM) algorithms with some extension to molecular dynamics propagators having the target of investigating the first released third-generation photochemically driven molecular motor (3GMs)
offering the possibility of transducing light energy into translational motions – at the nanoscale level – by means of excited state dynamics. The system is composed by the contextual presence of two rotating moieties (the rotors), two axes and a pseudoasymmetric stopper (see Scheme 1). UV/Vis absorption and time-resolved fluorescence measurements coupled with transient absorption measurements (TA) and femtosecond stimulated Raman spectroscopy in two different solvents (acetonitrile – ACN and cyclohexane – CHX) reveal detailed structural information following the absorption of photons in the range between 350–1200 nm. Photoexcitation has the effect of populating a vertical Franck–Condon “bright state” undergoing an ultrafast relaxation movement (within 300 fs) towards a much less-emissive intermediate dark-state. Afterwards the photo-molecular motor – passing through a conical intersection – returns in the singlet electronic ground-state featuring a much less-emissive intermediate dark-state. Afterwards, the molecular rotor passing through a conical intersection returns to electronic ground state in two different conformations: stable (initial) and meta-stable (the first intermediate of a unidirectional translational movement at nanoscale level).

In this contribution we report – for the first time – a theoretical and computational study focused on UV/Vis absorption processes of the 3GMs photo-molecular motor in dilute solutions as proposed by B. Feringa and co-workers. In particular, both the stable and meta-stable form reported in Scheme 1 have been addressed in terms of structural and electronic properties in ACN and CHX by means of quantum-mechanics based calculations with continuum and discrete solvent molecules. Moreover, our investigation has been extended including microseconds time scale molecular dynamics (MD) simulations in acetonitrile dilute solution with the target of addressing the effect of solvation environments and thermal fluctuations at room temperature on the electronic properties of the first proposed 3GMs. Our results shed some light on the conformational phase-space accessible under different conditions, and about the subtle and critical role that environmental effects can exert in modulating electronic degrees of freedom in complex molecular systems of potential interest for nano-technological applications.

Computational details

The molecular systems depicted in Fig. 1 were optimized at DFT level adopting different functionals while remaining within the Gradient Corrected Approximation (GGA) in conjunction with the 6-311+G** basis set; more precisely we considered the hybrid exchange–correlation Becke 3-parameters Lee–Yang–Parr (B3LYP) functional, its coulomb-attenuated version (Cam-B3LYP), the Perdew–Burke–Ernzerhof (PBE) functional and, at last, the PBE0 functional mixing the PBE exchange and Hartree–Fock (HF) exchange energy in a 3 : 1 ratio, along with the full PBE correlation energy. In addition, we used Grimme’s dispersion with the original D3 damping function as proposed in ref. 44. The systems were primarily relaxed by applying a redundant-based internal coordinates algorithm in gas-phase and subsequently in solution mimicking the ACN end CHX solutions by using the popular conductor-like polarizable continuum model (C-PCM) decomposition. The obtained geometries were then used as starting configuration to compute the UV-Vis absorption spectra at C-PCM/B3LYP(D3)/6-311+G** level of theory; moreover, the molecular orbitals involved in the Franck–Condon excitation processes were also analytically characterized in terms of electronic hypersurfaces superimposed over the optimized molecular structures. In addition, the optimized geometries were also characterized in terms of normal modes analysis (NMA). In this respect, the Gaussian 16 code (Rev. C01) was adopted for the computations herein reported.

As a next step, with the target of theoretically modelling – from a dynamical point of view – the lowest valence UV/Vis absorption bands experimentally detected at room temperature in ACN dilute solution, we have used a time-dependent (TD) approach over a QM/MM/C-PCM partitioning scheme as already proposed over similar molecular systems. A MD sampling was started considering the synthetic device at the centre of a cubic box having dimensions of 44 × 44 × 44 Å, and
the solvent molecules were modelled according to the classical parameters proposed by Van der Spoel and co-workers. At first, in line with experimental findings, we started the classical sampling with the motor in the stable conformation (see Scheme 1 and Fig. 1). The OPLS all-atom force field parameters were adopted and covalent bonds involving hydrogen atoms constrained using LINCS (linear constraint solver) algorithm. The MD sampling was carried out using GROMACS Software (release 2022.6). In practice, we considered a spherical cavity with a radius of 20 Å with the origin centred over the geometrical centre of the QM region, namely the artificial motor treated at Cam-B3LYP(D3) level. We then extracted from a room-temperature MD trajectory in NVT ensemble of 100 ns a snapshot every 4.0 ns, corresponding to 25 evenly spaced configurations. Subsequently, the explicit solvent molecules were considered within the perturbing classical (MM) region only in cases in which their COM distance was shorter than the imposed spherical cut-off. Furthermore, in the proposed simulation scenario, it is also important to remark that position restraints – with a force constant of $10^5$ kJ mol$^{-1}$ nm$^{-2}$ – are applied on each of the QM-based atoms to exclude solute dynamics effects. The investigated artificial motor was then modelled at QM level by using the 6-311+G** atomic basis set already applied in the presence of continuum model calculations. In so doing, in the proposed computational scenario, the investigated systems result confined within 25 different spherical nanodroplets in interaction with the solvent treated both by explicit molecules (treated as atomic point charges) and implicit ones (i.e., a spherical C-PCM cavity as described above).

Results and discussion

In Fig. 2 we report the optimized molecular structures as obtained considering the artificial molecular motor in dichloromethane dilute solution at C-PCM/Cam-B3LYP(D3)/6-311+G** level of theory. The same structures have been relaxed even at C-PCM/Cam-B3LYP(D3)/6-311+G** level of theory; we considered the phenyl group in two different orientations during the optimization process. The rotamer on the right panel is estimated to be more stable than other conformation in terms of standard free energy (see text).

In CHX solvent, the free energy difference between the two Phe-based rotamers of the simulated artificial rotor, always at C-PCM/Cam-B3LYP(D3)/6-311+G** level of theory, is found to be 3.45 kcal mol$^{-1}$ and +4.39 kcal mol$^{-1}$ using the B3LYP(D3) functional, respectively. For completeness we note that such an effect is principally due to steric effects since the C–C bond to the phenyl do not change its single-bond order character (the differences in terms of bond lengths remain confined between 1.543 and 1.547 Å).

The same computational approach has been applied considering the metastable structure (Fig. 1, right panel) which is found to be at higher standard free energy [Cam-B3LYP(D3): +7.80 kcal mol$^{-1}$ in ACN and 7.97 kcal mol$^{-1}$ in CHX]; [B3LYP(D3): +6.82 kcal mol$^{-1}$ in ACN and 6.87 kcal mol$^{-1}$ in CHX] when compared with the most stable conformation showing for both the solvents the Phe ring in an almost “parallel” orientation (Fig. 1, right panel) with respect to the rotating moieties.

Subsequently, considering the energetic profile defined above, we carried out TD-DFT computations involving different DFT functionals as reported in Section 2. The obtained UV/Vis absorption spectra in different simulation environments are shown in Fig. 3. At first, considering the most stable Phe-rotamer we observe that: (i) the B3LYP functional in ACN provides two distinct absorption signals lying at 496 nm and 397 nm wavelengths; (j) the PBE1PBE functional shows a similar behaviour with a maximum at around 488 nm and a second absorption band with a lesser intensity at 395 nm; (k) on the other hand, the Cam-B3LYP energetic profile results in better agreement with experimental measurements. As a matter of fact, the Cam-B3LYP unequivocally shows a main absorption band and a shoulder at shorter excitation wavelengths. Such a shape agrees with the spectroscopic measurements acquired in the laboratory. As a consequence, the Cam-B3LYP functional – with an absorption maximum falling at around 415 nm in ACN and a shoulder at 370 nm – provides a better reproduction of experimental data reported in literature in the same solvent an absorption maximum at 437 nm and a shoulder signal lying at around 390 nm; (l) at last, we have estimated that the pure DFT PBE0 functional tends to heavily overestimates the excitation wavelengths actually showing a first band at 535 nm and a second at almost 430 nm (see Fig. 3).
Extending the modelling to the other Phe-based rotamer, our data essentially suggest that, when the Phe ring in solution tends to assume conformations with an orthogonal orientation with respect to the rotating arms (Fig. 2, left panel) the UV/Vis excitation bands clearly undergo a systematic blue shift if compared with the excitations computed considering the most stable form. In fact, the Cam-B3LYP, B3LYP and PBE1PBE functionals show profiles with a similar shape (if compared with those computed in the most stable rotamer as shown in Fig. 3) and the main absorption band centred at 385 nm, 454 nm and 446 nm, respectively. Always remaining in this context, with the best performing functional, i.e. the Cam-B3LYP in this specific case – we also computed the absorption spectrum of the investigated molecular device in CHX for a direct comparison with data available in literature. The trend observed when comparing data in the two different solvents smoothly fits with the experimental observations. In fact, the UV/Vis absorption spectrum – at C-PCM/Cam-B3LYP(D3)/6-311+G** in CHX – shows a very similar profile with that previously estimated in ACN dilute solution showing slightly longer excitation wavelengths (see Fig. 2a reported in the electronic supplementary material in ref. 35). Moreover, we also introduced the metastable form in the prediction of the electronic excitations both in ACN and CHX solvents. The computed excitations – always at C-PCM/Cam-B3LYP(D3)/6-311+G** level of theory – reflects an absorption maximum band falling at longer wavelengths accordingly with experimental findings [485 nm in ACN and 490 nm in CHX (see Fig. 3) vs. 528 nm in ACN and 530 in CHX\(^{[35]}\)]. Lastly, for the sake of completeness, we report in Fig. 4 the relaxed potential energy surface scan along the dihedral angle connecting the two investigated Phe-rotamers in the electronic ground state at C-PCM/Cam-B3LYP(D3)/6-311+G** and C-PCM/B3LYP(D3)/6-311+G** level.

The rate determining “mechanical” transition state poised between the simulated rotamers is estimated to be accessible \emph{via} thermal energy fluctuations at room temperature. As a matter of fact, both the applied DFT GGA-based functionals estimate an energetic barrier lower than 1.9 kcal mol\(^{-1}\) (from left to right pathway): the Cam-B3LYP shows a potential energy barrier of 1.82 kcal mol\(^{-1}\) while the B3LYP a value of 1.54 kcal mol\(^{-1}\). The reverse rotational pathways display higher energetic barriers: 5.05 kcal mol\(^{-1}\) at C-PCM/Cam-B3LYP(D3)/6-311+G** level and 5.78 kcal mol\(^{-1}\) at C-PCM/B3LYP(D3)/6-311+G**. Moreover, ACN and CHX within the same DFT functional shows very similar potential energy profiles. In other words, our theoretical investigation let us suppose that, in ACN and CHX dilute solution at 298 K, the investigated molecular motor should preferentially assume conformations showing the Phe substituent within the pseudo-asymmetric unit in a different mutual position with respect to the already proposed modelling of the same system in ideal gas phase conditions.\(^{[35]}\)

Always remaining in this context and taking into consideration again the free energy data reported above, we can determine at C-PCM(ACN)/Cam-B3LYP(D3)/6-311+G** level of theory a ratio of probabilities of the two rotamers depending on the states’ free energy difference which suggests – on average – an almost 99.8% of molecules in the most stable form and the remaining ones in the other rotamer investigated. For the sake of completeness, we therefore recalculated based on this result the absorption bands reported in Fig. 3 and the best result obtained with the Cam-B3LYP functional has been displayed in Fig. 5. Given the negligible presence of the lesser stable rotamers in both the solvents (see Fig. 4), the obtained spectra in ACN and CHX dilute solutions result in line with
experimental observations explicitly reported in the inset of the same figure. In fact, the absorption maximum at C-PCM/Cam-B3LYP(D3)/6-311+G** for both the solvents substantially does not change its position remaining confined at 415 nm; in addition, even the shoulder lying at around 380 nm results in agreement with the experimentally observed detections if compared with the two separated UV/Vis spectrum reported in Fig. 3. Always intrigued by experimental analysis we have then focused our attention on the characterization of the so-called Franck–Condon “Bright” State (FCBS) following the excitation process and having a lifetime < 100 fs before relaxing to a much less-emitting dark-state intermediate. This FCBS is found to be emissive in nature with a broad fluorescence spectrum peaked at 580 nm. The computed – C-PCM/Cam-

B3LYP(D3)/6-311+G** – geometry in ACN reveals the strong vertical character of such a “Bright” state. The main structural change upon excitation is represented by an elongation of the covalent framework defining the rotational axes as a result of the π* character of the absorption [(Ground state; CC bonds = 1.357) (FCBS; CC = 1.406 Å)]. In this respect, a bond order analysis using natural bond orbitals (NBOs) essentially shows that such an excitation is accompanied by a symmetric reduction of the double bond character along the two rotating molecular axes. For the electronic ground-state, in line with not completely planar double bonds, the estimated bond order is found to be 1.75 while the same property on the FCBS surface features a value of 1.27. The estimated fluorescence spectrum is found to be emissive in nature with a broad fluorescence spectrum peaked at 580 nm. The computed – C-PCM/Cam-B3LYP(D3)/6-311+G** level of theory for both the solvents substantially agrees with the experimentally observed detections if compared with the two separate UV/Vis spectrum reported in Fig. 6 and 7, respectively.

The vertical absorptions in the energy range explored clearly evidence the predominant presence of 1π → π* excitation bands involving molecular orbitals from the HOMO−1 up to the LUMO+1 (where HOMO stands as usual for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital). When the stable form is concerned, the absorption band at longer wavelengths mainly provides a single HOMO → LUMO excitation character with a lesser extent of the HOMO−1 → LUMO+1 molecular orbitals (see Fig. 6). The shoulder signal typically blue shifted – both theoretically and experimentally – of almost 40 nm with respect to maximum in the range 300–600 nm basically reflects HOMO → LUMO+1 character. In addition, we would like to highlight that, the unoccupied molecular orbitals involved in the lowest 1π → π* excitations clearly display a nodal plane allowing photoisomerization along the C=C double bond connecting the rotating moieties themselves with the pseudo-asymmetric character of the absorption [(Ground state; CC bonds = 1.357) (FCBS; CC = 1.406 Å)]. In this respect, the TD-DFT procedure are reported in Fig. 6 and 7, respectively. A closer inspection of the molecular structure of the metastable product highlights that no further dissipative process can occur at nanoscale level. This basically because, at the same level of theory applied for the stable form (see data plotted in Fig. 4), the computed relaxed PESs along the Phe dihedral angle do not show the potential presence of other rotational isomers in ACN and in CHX dilute solution, respectively.

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molecular motor in explicit solvent molecules, are then used uncorrelated 25 evenly spaced configurations, showing the was analyzed extracting an MD snapshot every 4.0 ns. The classical simulation box and a MD trajectory of 100 ns in ACN at 298 K was performed. Subsequently, the classical MD trajectory would like to remark that, the position of the main absorption undergoes a moderate shift towards the experimental excitation and of 0.14 a.u. for the second one. Moreover, we would have been expected, the most stable rotamer (Fig. 2, right panel) shows \( \pi \rightarrow \pi^* \) excitation bands slightly modulated by bulk dielectric medium and interface solvation effects. The UV/Vis absorption spectra in the range 350–500 nm in ACN at 298 K, computed at Cam-B3LYP(D3)/6-311+G\( ^{**} \) + MM + C-PCM level of theory involving the two lowest valence \( \pi \rightarrow \pi^* \) absorption band for the stable form of the simulated motor (see Fig. 2). As explained in the text, the excitations (reported using dashed lines in grey colours) are computed using spherical nanodroplets hosting the artificial molecular motor and surrounded by a C-PCM cavity mimicking long range solvent electrostatic interactions. A nanodroplet hosting the investigated molecular rotor treated at Cam-B3LYP(D3)/6-311+G\( ^{**} \) level of theory is also shown in the inset. The profiles are obtained by combining excitation wavelengths with oscillator strengths and using Gaussian broadening functions with a full width at half maximum (FWHM) of 20 nm.

Finally, we then extended the present work addressing the perturbed electronic properties of the investigated system in the presence of thermal and discrete/continuum solvation effects in ACN at room temperature by adopting a QM/MM/C-PCM partitioning scheme in which explicit solvent molecules can change their position according to a classical MD propagator. As it was noted that, in line with typical QM/MM applications\(^{22,23}\) the electrostatic interactions are calculated from parametrized partial atomic point charges\(^ {49}\) changing their mutual positions following a classical molecular dynamics (MD) propagator. As it would have been expected, the most stable rotamer (Fig. 2, right panel) shows \( \pi \rightarrow \pi^* \) excitation bands slightly modulated by bulk dielectric medium and interface solvation effects. The lowest energy excitation essentially results confined in the range 420–415 nm – featuring a maximum lying at almost 418 nm – while the second valence \( \pi \rightarrow \pi^* \) excitation is found to sample wavelengths between 375 and 369 nm. On average, we estimate an oscillator strength of 0.70 a.u. for the first excitation and of 0.14 a.u. for the second one. Moreover, we would like to remark that, the position of the main absorption band undergoes a moderate shift towards the experimental value detected at 437 nm [from 415\( ^{\circ}\) (DFT+C-PCM)] nm to 418\( ^{\circ}\) (DFT+MM+C-PCM) nm]. Even the shoulder result is in line with the excitation data previously depicted in Fig. 3 and 5.

All in all, we observe that the spectroscopic data derived within

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**Fig. 7** Molecular orbitals, as extracted at C-PCM/Cam-B3LYP(D3)/6-311+G\( ^{**} \) level of theory, for the artificial molecular motor in the metastable form in ACN dilute solution. For the sake of clearness, the blue colour reflects the positive (+) counterpart of the corresponding eigenvector and an isodensity surface plot value of 0.015 e Å\(^{3} \) is represented.

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**Fig. 8** UV/Vis absorption spectra in the range 350–500 nm in ACN at 298 K, computed at Cam-B3LYP(D3)/6-311+G\( ^{**} \) + MM + C-PCM level of theory.
nanodroplets actually result in line with those previously computed by means of a state-of-the-art QM+C-PCM approach (see Fig. 3 and 5). This is basically because the moderate solvatochromic shift found in ACN is associated with $1\pi \rightarrow \pi^*$ electronic excitations accompanied by a moderate redistribution of the electronic density along the single-character excitation. Finally, it is worth noting that, test calculations carried out imposing larger spherical samples (cut-off distances of 22.0 Å and 24.0 Å) did not show significant differences in the excitation energies.

Conclusions

In this contribution we present a computational investigation focused on a recently released artificial molecular motor in two different solvents: ACN and CHX. The applied simulation workflow based on a quantum mechanical description of the motor with four gradient-corrected density functionals in conjunction with all-atoms molecular dynamics simulations supports the experimentally detected spectroscopic signatures. In this respect, the UV/Vis absorption patterns in dilute solution are reproduced and the resulting electronic excitations characterized in terms of valence $1\pi \rightarrow \pi^*$ molecular orbitals. We also considered the investigated synthetic device in the metastable product activated by photoexcitation dynamics evolving from a Franck–Condon bright-state through weakly emissive dark-state. The combination of a quantum mechanical modelling within the DFT framework with an implicit and polarizable solvation model leads to an UV/Vis absorption pattern for the investigated molecular rotor slightly underestimated if compared with the experimentally detected one. The current computational investigation sheds some light on the subtle and critical effects that electronic degrees of freedom and conformationally accessible structures can exert on the functional mechanisms of light-triggered molecular motors working in dilute solutions. Albeit not conclusive, we are confident that the present results might provide a useful starting point for future studies focused on this fascinating synthetic system while operating in exercise conditions and out of the equilibrium phases.

Author contributions

Costantino Zazza: investigation, data curation, methodology, software, writing – original draft, writing & editing, visualization. Stefano Borocci: supervision, conceptualization, methodology, visualization. Nico Sanna: visualization, supervision, project administration.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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