Calculations

Conducting Polymer Actuator Mechanism Based on the Conformational Flexibility of Calix[4]arene**

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The reversible electrochemical mechanism typical of conducting polymer actuators is based on the addition or removal of charge from the polymer backbone and a flux of ions into or out of the material to balance the charge.[1] Despite their impressive performance, these conducting polymer actuators, which can be envisaged as potential artificial muscles, are limited by the small conformational changes of the molecules, since polymer chains are not able to alter their length. In recent studies a new class of conducting polymer actuators based on conformational changes of the molecular chains rather than on the exchange of ions was developed.[2,3] The actuation mechanism of this material, which was constructed from small thiophene oligomers (quaterthiophenes) separated by calix[4]arene scaffolds (25,27-dihydroxy-26,28-dimethoxycalix[4]arene), namely, poly(calix[4]arene quaterthiophene), was explained in terms of reversible conformational changes produced by variations in the electronic structure of electrochemically activated polymer molecules (Figure 1).
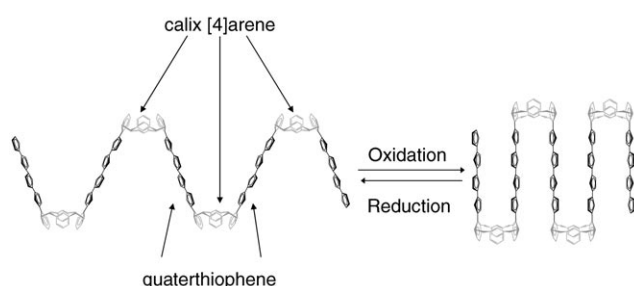

Figure 1. Schematic representation of the poly(calix[4]arene quaterthiophene) molecular actuator.

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Herein we prove that the molecular actuation mechanism of this material is driven by repulsive electrostatic interactions involving the calix[4]arene scaffolds rather than by attractive π–π stacking interactions between quaterthiophene units as was recently suggested.[3,4]

Computer studies based on different simulation techniques have been used to obtain accurate and detailed microscopic information. It should be noted that atomistic modeling is currently considered to be a powerful tool for studying the structure and properties of polymeric materials.[5] Both quantum mechanical calculations and classical molecular dynamics simulations reported in the current study support the flexibility of the calix[4]arene units being the main cause of the surprising ability of poly(calix[4]arene quaterthiophene) to be deformed.

Figure 2 shows one actuating unit of poly(calix[4]arene quaterthiophene) in the reduced, oxidized-nondeprotonated, and oxidized-deprotonated states (hereafter abbreviated Red., Ox-Ndep, and Ox-Dep, respectively) after full structural and electronic relaxation by using quantum mechanics analyses. Calculations were performed that allowed oxidation of the two quaterthiophene segments, while deprotonation occurred at the two hydroxy groups of the 25,27-dihydroxy-26,28-dimethoxycalix[4]arene scaffold. It should be emphasized that experimental evidence indicated the presence of nondeprotonated and deprotonated forms after oxidation of the fully reduced state,[3] which justifies the study of both the Ox-Ndep and Ox-Dep forms.

Oxidation produces an expansion of 9.03 Å. This is a very reasonable result since the main interaction in the Ox-Ndep species is the electrostatic repulsion between charged quaterthiophene units. Previous studies using bithiophene as a model compound indicated that the electrostatic repulsion of two radical cations is very high: about 50 kcal mol^{-1} at distances of 5 Å.[6] Thus, the conformational flexibility of the calix[4]arene scaffold, which arises mainly by the rotation of an oxygen atom through the annulus, alleviates the repulsive interaction between the charged quaterthiophene units by expanding the system. It should be noted that recent studies[7,8] proved the conformational flexibility of calix[4]arenes, in particular of 25,27-dihydroxy-26,28-dimethoxycalix[4]arene.[8]

On the other hand, deprotonation produces a dramatic contraction of 30.37 Å, which is in agreement with experimental observations.[2–4] It should be noted that no restriction was imposed during optimization of the geometry, the starting structure being that of the Ox-Ndep species. The origin of this drastic contraction is the electrostatic repulsive interaction between the charged atoms of the phenolate rings, which is partially reduced

by increasing the distance between them. This effect is illustrated in Table 1, which compares the O···O distances of the three states shown in Figure 1 with those obtained for 25,27-dihydroxy-26,28-dimethoxycalix[4]arene and its deprotonated form. As can be seen, the O···O distance increases by 2.705 Å when the two hydroxy protons of the oxidized actuating unit are removed. This expansion brings the two oxidized quaterthiophene units nearer, with the repulsion between the two radical cations being alleviated by the
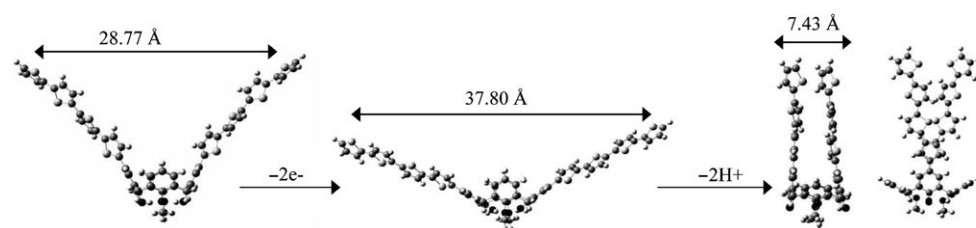
Figure 2. Optimized structure of one actuating unit in the Red. (left), Ox-Ndep (middle), and Ox-Dep (right) states. The distance between the ends of the two quaterthiophene oligomers is indicated. The deprotonated-oxidized form is displayed in two different orientations to illustrate the scissor-shaped arrangement of the quaterthiophene oligomers.

Table 1: Distance[a] between the oxygen atoms of R^2 for the actuating unit (Figure 1) and 25,27-dihydroxy-26,28-dimethoxycalix[4]arene in different states.
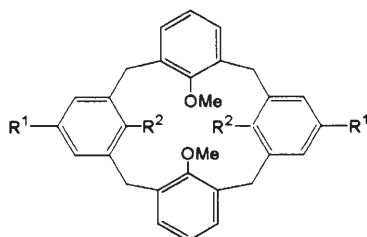
Compound	State	O⋯O [Å]
actuating unit		
R^1 = quaterthiophene, R^2 = OH	Red. (neutral)	4.276
R^1 = quaterthiophene⁻⁺, R^2 = OH	Ox-Ndep	3.196
R^1 = quaterthiophene⁻⁺, R^2 = O⁻	Ox-Dep	5.901
25,27-dihydroxy-26,28-dimethoxy-calix[4]arene		
R^1 = H, R^2 = OH	nondeprotonated	4.357
R^1 = H, R^2 = O⁻	deprotonated	5.575

[a] Results obtained from HF/6-31G(d) (non-oxidized species) and UHF/6-31G(d) (oxidized species) geometry optimizations.

adoption of a scissor-shaped arrangement (Figure 1). Furthermore, the O⋯O distance for the Ox-Dep actuating unit and the deprotonated 25,27-dihydroxy-26,28-dimethoxyca-lix[4]arene differ by only 0.326 Å. This similarity indicates that the repulsion between the two charged oxygen atoms of the calix[4]arene moiety is crucial for explaining the remarkable geometric changes observed upon deprotonation of the charged actuating unit (Figure 2).

Classical molecular dynamics (MD) simulations of a system consisting of six calix[4]arene scaffolds separated by five quaterthiophene units (Figure 3) were performed in both the gas phase and in CH₂Cl₂ solution for the Red, Ox-Ndep, and Ox-Dep states. Figure 3
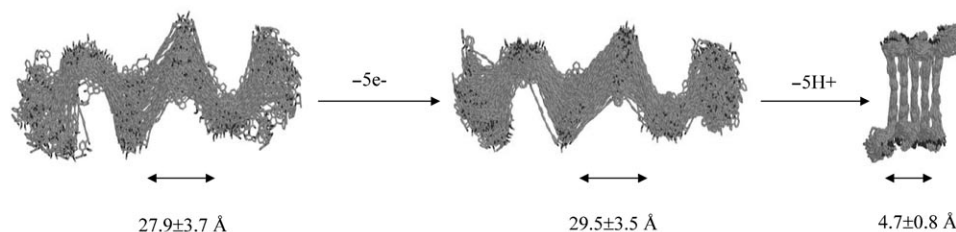
shows snapshots of each simulated system at 10-ps intervals over the 10 ns of the MD simulation in solution, with the average distance calculated between the ends of the quaterthiophene oligomers belonging to the same actuating unit also displayed.

As can be seen, the results obtained using classical molecular dynamics calculations are fully consistent with those predicted by quantum mechanical calculations. Thus, oxidation of the quaterthiophene oligomers produced an expansion, while deprotonation of the oxidized species led to a dramatic contraction. It should be noted that the force-field parameters used in these simulations were derived explicitly for each species, taking into account the charge of the quaterthiophene oligomers and/or the deprotonation of the calix[4]arene unit. Despite this, the distance between the ends of the actuating unit derived from classical simulations differs quantitatively, although not qualitatively, from those obtained using quantum mechanics. This situation can be attributed to different reasons, the most important being: 1) the use of fixed force-field parameters in MD simulations, that is, electronic relaxation effects are neglected; 2) an isolated actuating unit is considered in quantum mechanical calculations whose conformational flexibility is expected to be higher than that of a unit linked to neighbors in a polymer; and 3) the omission of anionic counterions in quantum mechanical calculations, which are expected to mitigate the repulsive electrostatic interactions.

It was recently suggested that the π–π stacking between the thiophene oligomers is the driving force for molecular actuation of poly(calix[4]arene quaterthiophene).[4] Thus, the contraction of the material was attributed to the formation of stable dimers of oxidized quaterthiophenes in solution, while the conformational flexibility of the calix[4]arene was only used to explain the accordion-like molecular displacement. In this study we have analyzed both Ox-Ndep and Ox-Dep forms by using different theoretical methods in both gas-phase and solution environments. The overall results lead to the conclusion that the electrostatic repulsions between the charged atoms of the calix[4]arene scaffolds are responsible

Figure 3. Superposition of snapshots recorded from classical molecular dynamics simulations of a system constituted by five actuating units in the Red. (left), Ox-Ndep (middle), and Ox-Dep (right) states in CH₂Cl₂ solution. The average distance between the ends of the two quaterthiophenes belonging to the actuating unit is indicated.

for the reduction in the length of the poly(calix[4]arene quaterthiophene) chains. Thus, conjugated quaterthiophene segments should not be considered to be the main active elements in the molecular actuation mechanism, even though their electrochemical oxidation is essential to promote the deprotonation of the calix[4]arene unit and to control the conductivity of the polymer. It is hoped that the proposed actuation mechanism will help in the design of optimized molecular devices containing calix[4]arene scaffolds.

Experimental Section

Ab initio quantum mechanical calculations were performed on calix[4]arene, 25,27-dihydroxy-26,28-dimethoxycalix[4]arene, and one actuating unit formed from two quaterthiophene oligomers attached to a calix[4]arene scaffold. Full geometry optimizations were carried out at the Hartree–Fock level using a 6-31G(d) basis set.[9] Calculations on the oxidized actuating unit were performed considering the unrestricted quantum-chemical formalism with triplet spin multiplicity, that is, allowing oxidation of the two quaterthiophene oligomers.

Classical MD simulations were performed with the NAMD2.0 program,[10] with an integration step of 2 fs selected. The bond geometries that involved non-hydrogen atoms were kept at their equilibrium distances as obtained by using the SHAKE algorithm.[11] Electrostatic interactions were extensively computed by means of Ewald summations. The real space term was defined by the van der Waals cut-off (14.0 Å), while the reciprocal space was computed by interpolation into an infinite grid of points (Particle Mesh Ewald), with a grid density of 5.0 points $Å^{-3}$. Sets of partial atomic charges were derived explicitly for all the investigated species taking into account the electronic state of the thiophene oligomers. Equilibrium bond lengths and angles for the latter were derived from quantum mechanical geometry optimizations on one actuating unit. Simulations were performed with a fixed all-*anti* conformation of the quaterthiophene oligomers, independent of their electronic state. The force-field parameters required for the calix[4]arene scaffold[12] and the CH_2Cl_2 solvent[13] were taken from the literature. The counterion used in simulations of the Ox-Ndep form was PF_6^-, which was recently parametrized.[14]

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