Light-Activated Molecular Conductivity in the Photoreactions of Vitamin D_3

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In this theoretical−experimental approach, we show using ab initio calculations behavior consistent with the activation of 7-dehydrocholesterol, provitamin D_3, as an initial reactant toward ultraviolet-activated reactions of vitamin D_3. We find using molecular orbital theory that a conformation between the provitamin and the vitamin shows higher conductance than those of the reactant and product. We also find experimental evidence of this electrical character by directly measuring current−voltage characteristics on irradiated and nonirradiated samples of the provitamin. The activation of the provitamin D_3 is characterized with an increase in current during the irradiation.

1. Introduction

The mainstreaming of personal computers and the surge in use of handheld digital devices such as cellular phones have been accompanied by a continued demand for faster, more versatile electronic circuits. On the forefront of research in this area is nanotechnology—designing and fabricating nanosized electronic components that provide increased functionality compared to current silicon-based technologies while occupying a fraction of the size. One promising solution for scaling down electronic devices below the present limits of photolithography is the molecular circuit. Understanding and manipulating molecular conductivity is one of the initial steps in the development of such circuits,[1−4] and this requires knowledge of a particular molecule's electrical character. Indeed, many organic and biological molecules with conductive properties have been examined as potential circuit elements.[5−7] Of even more interest are light-sensitive molecules with conductive character. A molecule whose electrical conductance changes in response to light is an excellent candidate for light-activated circuits.

One light-sensitive biological molecule of interest is 7-dehydrocholesterol (provitamin D_3), which, upon exposure to ultraviolet (UV) light in the range of 240−300 nm,[8] undergoes photoconversions that lead to the production of cholecalciferol (vitamin D_3). These reactions occur in the skin, naturally providing the body with a supply of this vitamin. Its physiological importance has been established; vitamin D is known to offer protective effects against the development of cancers of the breast, colon, prostate, lung, and ovary[9,10] and the therapeutic intervention and prevention of many disorders including diabetes and osteoporosis.[11]

Through extensive studies using various cellular and liposomal models, the production of vitamin D_3 in the epidermis is currently well-understood.[12−17] An equal effort has been given in characterizing these photoreactions outside the body through experimental[18−22] and, more recently, computational techniques.[23−26] Through their analyses, many have contributed to a more complete understanding of the photochemical process at each stage and of the factors—solvent and wavelength, in particular—that influence the progression through subsequent stages.[8,27−30]

Neither the electrical properties of the molecules in these photoreactions nor their potential usage in a biomolecular circuit has yet to be considered. No one has explored the ability to maximize any useful electrical properties by controlling provitamin D conversion and eliminating the undesired side products that result from overirradiation.[31]

Therefore, in this work, we use ab initio methods to evaluate the practicability of using the conductivity characteristics of the moieties formed during the photoreactions of vitamin D_3 and experimentally measure the current−voltage characteristics as a proof-of-concept. In the next section we describe the theoretical and experimental methodologies, and then the following one explains the results. Finally the last section summarizes the conclusions.

2. Methodology

Calculations. The energies and geometries of the molecules participating in the photoreaction of vitamin D_3 are calculated with first-principles density functional theory using the program Gaussian 03[32] by means of the B3PW91 hybrid functional which uses the fully nonlocal Becke 3 (B3) exchange functional and a combination of the generalized gradient approximation (GGA) and the GGA Perdew−Wang 1991 (PW91) correlation functional with the 6-31G* basis set.[33−35] This level of theory has been successfully tested to yield acceptable energetics.[36] Electron transport is calculated using our program GENIP-07,[37−39] which calculates current through molecules using an ab initio density functional theory for the discrete and continuum components of the system, to merge through a Greens function approach.

Experiment. We prepare a solution of provitamin D_3 (∼2 mM) in a nitrogen atmosphere by dissolving crystalline 7-dehydrocholesterol in cyclohexane (≥99%). Both are obtained from Sigma-Aldrich and are used as received from the vendor. By using a micropipet, we deposit 4 μL of this solution onto a borosilicate biochip patterned with gold array microelectrodes (ABTECH Scientific, Inc.) shown in Figure 1a. The chip is dried under nitrogen for ∼3 h and then transferred to the measurement chamber of a TTP4 Cryogenic Probe Station (Desert Cryogenics, LLC) shown in Figure 1b. We connect the probe tips to the

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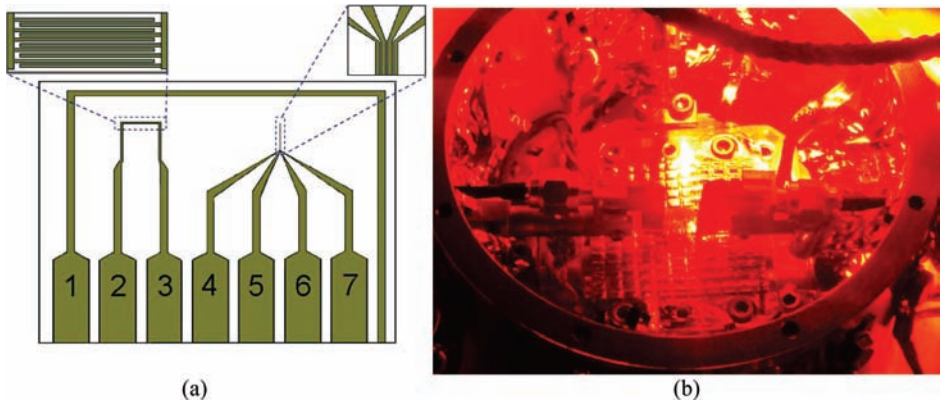

Figure 1. (a) The IAME-co-IME series chip from ABTECH Scientific, Inc., is used for the experiment. It contains a total of seven gold electrodes distributed in two different configurations: electrodes 2 and 3 are the interdigitated microsensor electrodes (IME) configuration and 4, 5, 6, and 7 are the independently addressable microband electrodes (IAME) configuration. The chip dimensions are 1.0 cm × 1.0 cm × 0.05 cm. Each electrode is 3 mm long, 2 μm wide, with 1 μm spacing between electrodes. Adapted from Abtech Inc. (b) TTP4 Cryogenic Probe Station (Desert Cryogenics, LLC).

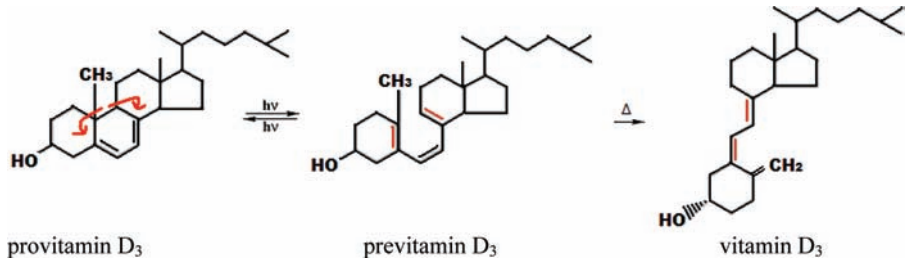

Figure 2. Simplified photoreactions of vitamin D_3 showing the molecules analyzed in this work. The red arrows show that the single bond in provitamin D3 is broken to form the red bonds in the previtamin D_3.

TABLE 1: Energies, Relative Energies, Dipole, HOMO and LUMO Energies, and HOMO−LUMO Gaps

molecule	energy (Ha)	relative energy (kcal/mol)	dipole (D)	HOMO (eV)	LUMO (eV)	HLG (eV)
provitamin D_3	−1130.182971	0.0	2.02	−5.26	−0.41	4.85
previtamin D_3	−1130.038827	90.5	1.61	−3.37	−2.29	1.08
vitamin D_3	−1130.162394	12.9	1.49	−5.31	−0.69	4.62
tachysterol	−1130.174090	5.57	1.78	−5.17	−0.69	4.35
lumisterol	−1130.162776	12.67	1.34	−5.21	−0.81	4.46
cyclohexane	−235.799891		0.00	−7.95	2.56	10.50

interdigitated microsensor electrodes (IME) portion of the chip (Figure 1a), and bias voltages are applied across the electrodes using a semiconductor analyzer. We apply voltage in two ways—swept linearly from −1 to 1 V and at constant steps of 1 V. During alternate applications of constant voltage, we expose the chip to UV light of wavelength 254 ± 10 nm obtained from a 4 W peak power lamp (90% efficiency) with a filter centered at 254 nm and with a bandwidth of 30 nm (handheld UV lamp from LDP, LLC) for 80 s intervals. Output dc values are measured simultaneously and are presented in time-domain plots. We repeat this procedure until the measured current values indicate complete photoconversion of the initial 7-dehydrocholesterol. Identical current measurements are made for a new, clean biochip and one covered with 4 μL of cyclohexane. All phases of the experiment are conducted under darkroom conditions at 298 K and 1 atm of pressure.

3. Results and Discussion

Figure 2 shows the initial provitamin D_3 molecule, its immediate UV product previtamin D_3, and the final product vitamin D_3, which result from thermal stabilization rather than from further UV exposure. Figure 2 does not show the additional photoproducts that result from overirradiation of previtamin D_3 such as the ring-closure product lumisterol, which is favored at wavelengths above 300 nm, and tachysterol, a product resulting from cis−trans isomerization that is more probable at smaller wavelengths.[21] Further wavelength-dependent side products are generated from the overexposure of vitamin D_3.[28]

The relative and total energies of the molecules in the simplified reaction scheme are shown in Table 1. The intermediate conformation is 3.92 eV (90.5 kcal/mol) above the provitamin and the vitamin is only 12.9 kcal/mol above. From Table 1 and Figure 4, we notice that the highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) gap (HLG) for the initial (provitamin D_3) and final product (vitamin D_3) of the photoreaction are 4.85 and 4.62 eV, respectively, whereas the molecular transition conformation (previtamin D_3) has a shorter HLG of 1.08 eV.

Figure 3 shows the current−voltage curves calculated using our in situ developed program GENIP.[37−39] In contrast with the experimental findings, higher conductivity is found for the final stage vitamin D_3 compared to that for the initial state provitamin D_3. We attribute this difference to the side products formed by the long exposure periods able to activate those states below the tail on the onset of the UV lamp spectrum such as tachysterol and lumisterol formed in photoreactions with wavelengths of about 295 nm.[21] Because of the low stability of previtamin D_3, its calculation under a current−voltage approach is really a

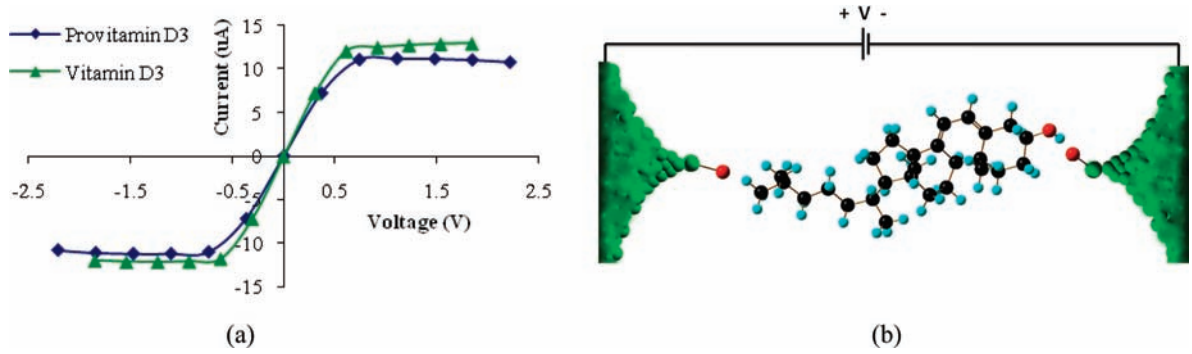

Figure 3. (a) Current−voltage characteristics for the provitamin D_3 and the vitamin D_3 obtained using GENIP. The differences in current are approximately 2 μA. (b) Schematic representation of the contact between the studied single molecules and the gold electrodes (green); physical adsorption is assumed through hydrogen bonding. The calculations refer only to a single molecule addressed by two electrodes; certainly, in the experimental setting, a random distribution of vitamin contaminated with side products is expected with the ends of the random sample (not each molecule) connected to the electrodes. Thus, calculations and experiment are at most complementary in their results in order to analyze several aspects of the system rather than to make validations of each other.

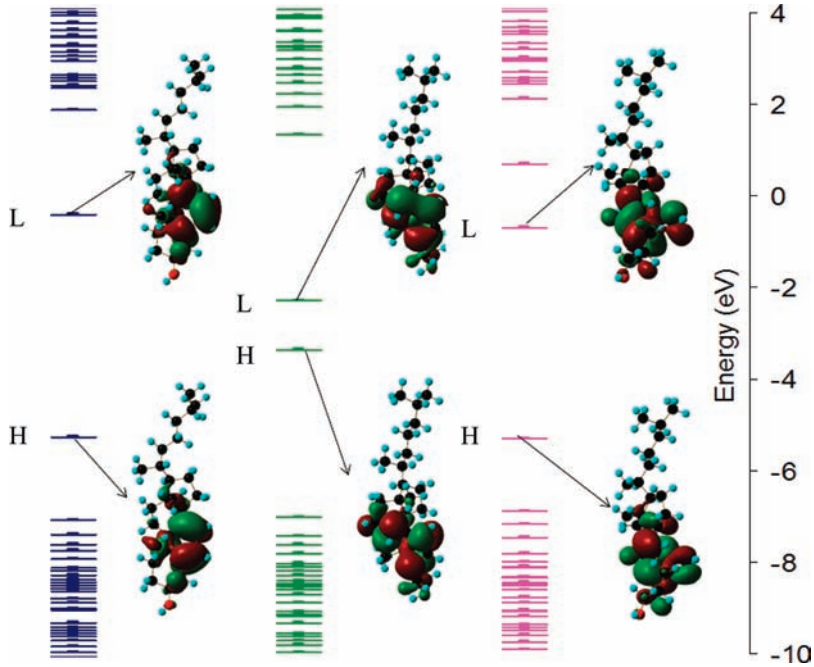

Figure 4. Molecular orbitals of provitamin D_3 (blue), previtamin D_3 (green), and vitamin D_3 (pink). LUMO (L) and HOMO (H) shapes and energies are shown; only energies are shown for the other MOs.

challenge and perhaps beyond what present methods can calculate. Self-consistent field calculations are superb for stable molecules but very problematic, as expected, for unstable ones. Short HOMO−LUMO gaps, i.e., low hardness, are indicative of poor stability of the wave function, which worsens as an external field is applied to the molecule.

The UV light in the experiment has a wavelength of 254 ± 10 nm, which corresponds to an energy range of 4.70−5.08 eV. Thus, the photons from the UV source provide the energy to excite an electron from the HOMO to the LUMO (4.85 eV) of provitamin D_3, which in turn yields to the intermediate conformation (previtamin D_3) at 3.92 eV above. The provided energy breaks the bond of one ring as is shown in Figure 2 and consequently stabilizes in vitamin D_3. The HLG at the transition conformation decreases but it is actually a local minimum as the reactant and the product are. The energies of the molecular orbitals are shown in Figure 4. The shapes of the HOMO (H) and LUMO (L) for the three molecules in the photoreaction show localizations in the neighborhood of the three adjacent six-member carbon rings in which the photoreactions take place.

Previtamin D_3 and vitamin D_3 both have the HOMO (Table 1) closer to the Fermi level (−5.3 eV) of the gold contacts, according to molecular orbital theory. The localization of the molecular orbitals (MOs) on the rings of the molecules and their HOMO−LUMO gaps suggest poor conduction with a transport path expected through nonbonded sites connecting the double bonds. Experimentally, a self-assembled monolayer physically absorbed in the glass substrate is expected. To make sure that no other MOs are strongly involved in the conduction process, we calculate the shape and energies of the HOMO-1 and HOMO-2; they show the same degree of localization as the HOMO (shown in Figure 4) but at larger energy separation (1.55 eV or more) than the HOMO energy from the Fermi level. This explanation taken from molecular orbital theory is much more suitable than the electron−hole models from solid state theories in which the conduction could be regarded as "electron" conduction as opposed to "hole" conduction.

Figure 5a shows the experimental current response of the chip when a constant voltage of 1 V is applied between the metallic contacts. A reversible decrease in current is observed before

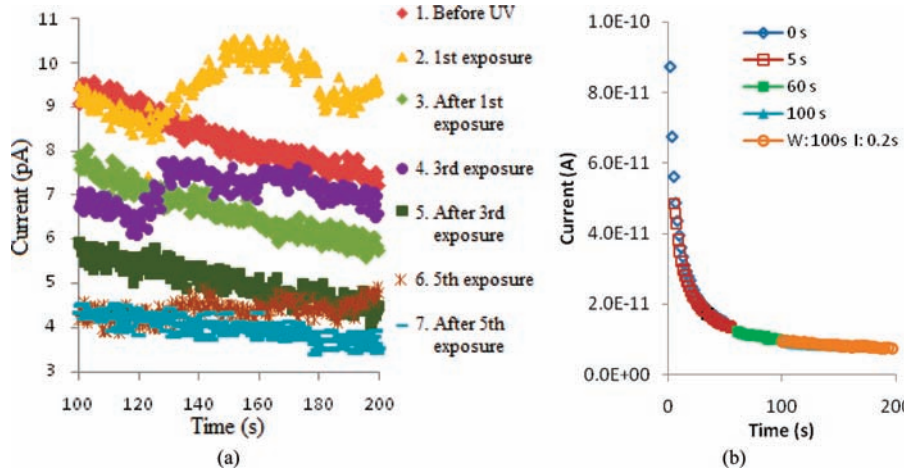

Figure 5. (a) Current responses when a constant voltage of 1 V is applied to electrodes 2 and 3 of Figure 1 using a wait time of 100 s during a time interval of 0.5 s. The total time for each consecutive measurement is 6.3 min. The exposure to UV starts at 120 s of voltage application and continues until 200 s. (b) Current versus time plot for the provitamin D_3 before irradiation using different wait times (voltage application time before start of measurement); the results presented in (a) follow the orange curve (from 100 to 200 s) where the change in current was 0.02 pA/s. Thus, no matter how many times we repeat the experiment, the $I-V$ behavior is exactly the same as long as the sample is not irradiated. Notice in (a) that the behavior is different when the sample is exposed to UV radiation (curve 2). The UV exposure is repeated five times, until no more changes in the current are detected.

the application of UV light as is shown in Figure 5b. Immediately upon UV exposure, the current increases to a maximum and then decreases in a manner similar to that when the UV source is off. This behavior is observed only when the chip is covered with the provitamin D_3 solution, i.e., when the solvent is completely evaporated and only the provitamin D_3 molecules are filling the gaps between the electrodes. The current responses for both the clean chip and the chip covered with only solvent are measured under the same irradiation conditions used for the provitamin D_3. Neither the chip nor the solvent displays the electrical behavior observed when the provitamin is present. Thus, we can confidently assign the peak in the current that accompanies UV exposure to the provitamin D_3 molecules. In the experiment a change of 5 pA is measured between the initial and final stage, such small current values can be measured with standard complementary metal oxide semiconductor electronics.

The gradual decreasing current response observed after UV exposure is unexpected from the HLG of the molecules in the simplified reaction scheme. Because of their similar HLGs and shape of molecular orbitals, we could expect the initial and final resistivities to be also similar.

Additional photoproducts, based on our experimental approach (i.e., long UV exposure times), are guaranteed to be present, for example, lumisterol and tachysterol, which are not shown in our analysis. However, we found properties very similar to those of the vitamin D_3, and the presence of the additional photoproduct molecules can account for the change in resistivity as the provitamin D_3 molecules undergo photoconversion.

A possible change in the orientation of the molecules from a higher order in the case of the provitamin due to its larger dipole moment to lower order in the vitamin due to its 25% lower dipole that may carry out the decrease in conductivity in the final stage is not ruled out.

Control experiments such as pure reaction compounds and mixtures can be performed; however, the information we would obtain in a control experiement is already available as only the first measurement corresponds to pure provitamin D_3; all other measurements correspond to a mixture of provitamin D_3, vitamin D_3, and side products. These measurements were needed to analyze provitamin D under UV irradiation.

We expose the sample five times to the UV light. Figure 5 shows the first, third, and fifth exposures. During the third exposure a change in current occurs when the UV is turned on and the switching behavior is smaller each time that the UV is turned on and after the fifth time when no change in current is observed, which we attribute to the end of the photoreaction, when all the provitamin D_3 has reacted and no more previtamin D_3 appears when the light is on.

4. Conclusions

We have shown by a theoretical−experimental ab initio based approach the activation of 7-dehydrocholesterol, a provitamin D_3, as an initial conformation toward ultraviolet-activated reactions of vitamin D_3. A molecular conformation between the provitamin and the vitamin is found with higher conductance than those of the reactant and product. We also find experimental evidence of this electrical character by directly measuring current−voltage characteristics on irradiated and nonirradiated samples of the provitamin. The activation of the provitamin D_3 is characterized with an increase in current during the irradiation. Energetics of the conformations and electronic structure suggest behavior consistent with the experiment which shows a molecular switch by its change in conductivity triggered by ultraviolet radiation of energy similar to that calculated theoretically for the molecules. It is also proposed that on the basis of the dipole moment we can explain the behavior of the reactant and product which happen to have most other similar characteristics but the dipole, which strongly affects intermolecular order.

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