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π-Dimer Formation as the Driving Force for Calix[4]arene-Based Molecular Actuators

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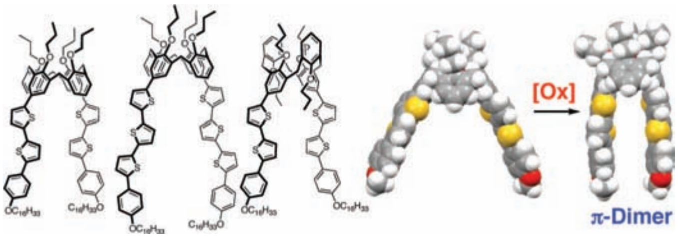
ABSTRACT



Stable π-dimers are formed upon oxidation of the model units of proposed calix[4]arene-based molecular actuators in a solvent of low dielectric constant (CH_2Cl_2) at room temperature. Evidence from UV−vis, EPR, and DPV are all in agreement with the π-dimer formation. In addition, π-dimer formation is dependent upon the conformational flexibility of the calix[4]arene hinge.

Conducting polymer (CP) actuators can change dimensions in response to electrochemical stimulation.[1,2] They are particularly attractive because of their light weight, low driving voltages, and processibility. The accepted mechanism for actuation in conducting polymers is the so-called "swelling mechanism", in which a volume change of bulk materials is caused by uptake or release of counter-ions and accompanying solvent molecules upon oxidation or reduction.[1] A complementary approach is to design molecular actuators, which are materials having geometrical changes at the molecular level to create dimensional changes. It should be noted that unlike bulk actuators (e.g., polypyrrole), polymeric molecular actuators seek to harness dimensional variations resulting from changes in the backbone structure of a polymer. We envision that if we utilize the conformational changes of single polymer chains, we may obtain faster responses and larger strains, which can enable the bottom-up development of nanodevices and machines.

Our group designed a calix[4]arene-based molecular actuator (Figure 1a), in which electroactive oligothiophenes are connected by the calix[4]arene scaffold.[3] We proposed that each calix[4]arene moiety acts as a molecular hinge and that new noncovalent interactions between oxidized oligothiophenes (i.e., π-dimer or π-stack) can drive the dimensional changes. The π-dimer involves the nonconventional multicenter bonding between cofacial radical cations, and this interaction has drawn particular attention as a model for interchain bipolarons as charge carriers in conducting polymers.[4] π-Dimer formation has been demonstrated in solution

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(1) Baughman, R. H. *Synth. Met.* **1996**, *78*, 339–353.

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(3) (a) Anquetil, P. A.; Yu, H. -h.; Madden, J. D.; Madden, P. G.; Swager, T. M.; Hunter, I. W. *Smart Mater. Struct.* **2002**, *4695*, 424–434. (b) Yu, H.-h.; Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 1142–1143. (c) Yu, H. -h.; Swager, T. M. *IEEE J. Oceanic Eng.* **2004**, *29*, 692–695.

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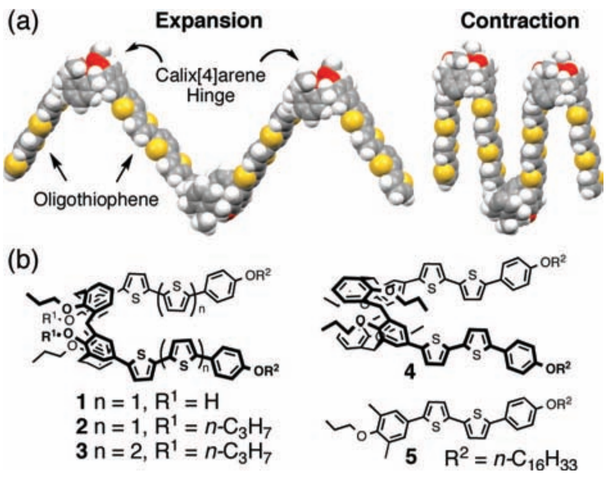


Figure 1. (a) Schematic description of the calix[4]arene-based molecular actuator. (b) Model compounds (**1**−**4**) used in this study and a reference molecule (**5**).

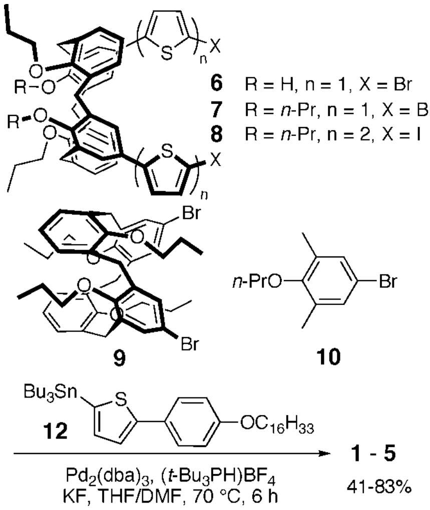
and in the solid state for oligothiophene derivatives.[5,6] In order to take advantage of such interactions as a driving force for molecular actuators, we considered that a segmented polymer would be more suitable than a fully conjugated one because it is able to attain larger interactions due to the spatial confinement of the radical cation's wave functions. More diffuse radical cations will necessarily result in weaker orbital interactions in these dimeric structures. It should be noted, however, that higher degrees of spatial confinement can result in Coulombic repulsion of like charges, and counterions are likely to play a major role.

The ab initio calculations by Scherlis and Marzari modeling one actuating unit supported the concept that π-stacking between oxidized oligothiophenes induces conformational changes.[7] They utilized 1,3-alternate calix[4]arene hinges, which are more flexible than the cone conformation, and found that a mixed-valence complex exhibits π-dimer bonding interaction in the gas phase. Interestingly, Casanovas and co-workers reported a different actuation mechanism.[8] On the basis of calculations, they concluded that oxidized oligothiophenes do not interact each other due to Coulombic repulsion of like charges. Instead, they suggested that for the calix[4]arene scaffold deprotonation can drive the conformational change.

It is clear that the stacking behavior of oxidized oligothiophenes is greatly affected by solvation and counterion screening.[9] In addition, π-dimer formation is greatly enhanced if oligothiophenes are connected by a linker.[5c,d] Therefore, we thought π-dimer formation was still a viable mechanism, and we present herein a series of model studies that support the hypothesis that π-dimer formation can indeed be a driving force for the calix[4]arene-based molecular actuator.

To conduct model studies of the actuating unit, we synthesized **1**−**4** (Figure 1b), which contain a calix[4]arene hinge and two oligothiophene derivatives as electroactive segments (Scheme 1). First, we sought to examine which, if any, of these compounds would give rise to stable radical cations when oxidized and whether π-dimer formation would take place. Second, the effect of the calix[4]arene's conformation (cone vs 1,3-alternate) was the subject of investigation.

Scheme 1. Synthesis of Model Compounds **1**−**5**



We examined several oxidizing agents to produce radical cations of **1**−**5** and finally chose Et_3OSbCl_6, a Meerwein's salt, as a 1-electron oxidant[10] (not as an alkylating agent) because it is relatively easy to handle and, more importantly, it does not exhibit a strong absorbance above 300 nm in the UV−vis spectrum. Therefore, we were able to monitor the diminution of the neutral absorption and the concurrent evolution of new absorptions without any interference (Figure 2a−c). Upon addition of the oxidant, all oligothiophenes were converted to deep-blue or violet radical cations, which were stable to moisture. However, the color was slowly lost (returned to the neutral state) when air was bubbled through the solution.

For the oxidation of monomeric **5** in CH_2Cl_2 under ambient conditions (Figure 2c), the initial $\pi-\pi^*$ absorption (382 nm) decreased and new peaks (645, 1079 nm) developed, which can be attributed to the polaronic absorptions (radical cations).[11] These sub-bandgap transitions with vibronic structures are in good accord with literature precedents.[5,12] We were not able to observe the formation of dications even

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(6) Kingsborough, R. P.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 8825–8834.

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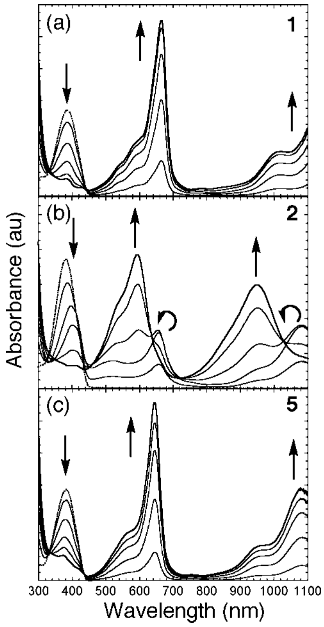

Figure 2. UV−vis spectral changes of **1** (a), **2** (b), and **5** (c) in CH_2Cl_2 at room temperature upon the increasing addition of the oxidant Et_3OSbCl_6. Spectra of neutral absorptions are displayed by dashed lines.

after adding excess amounts of Et_3OSbCl_6 under the above conditions.

Remarkably distinct behavior was observed upon oxidation of **2** (Figure 2b). Polaronic peaks, similar in shape to those of $\mathbf{5}^{\bullet+}$, were dominant at the low levels of oxidation. However, as more oxidant was added, blue-shifted absorptions were evident. Such blue shifts are characteristic of π-dimer formation.[5] The same phenomenon was observed upon oxidation of **3**, the terthiophene-substituted version (Supporting Information). It was expected that the longer oligothiophene forms stronger dimers, probably due to the reduced Coulombic repulsion.[5c] The results of the present study are noteworthy in that a stable π-dimer is generated at room temperature in a solvent of low dielectric constant (CH_2Cl_2) from a framework as short as two thiophenes.

Interestingly, when we added the oxidant Et_3OSbCl_6 to **1**, only polaronic absorptions were observed in the UV−vis spectra (Figure 2a). The only difference is that **1** has free hydroxyl groups at the lower rim of the calix[4]arene moiety.[13] We attribute this reluctance to form a π-dimer to the calix[4]arene's conformational rigidity resulting from lower-rim hydrogen bonding. However, it should be noted here that the π-dimer formation is coupled to the "motional" flexibility of the calix[4]arene hinge (hydrogen-bonded vs tetraalkylated).

The effect of the calix[4]arene's conformation on the dimer formation appeared minimal. Oxidation profiles of 1,3-alternate **4** are very similar to those of cone **2** (Supporting Information). The conformation of **4** is fixed because propyl groups or larger substituents are too large to rotate through the annulus of the calix[4]arene macrocycle at room temperature.[14] Therefore, it is unlikely that there is an interconversion of **4** to **2** and vice versa. We can conclude that the cone and 1,3-alternate conformations of **2** and **4** are sufficiently flexible to allow π-dimer formation when oxidized. Table 1 summarizes the absorption maxima of **1**−**5** in their neutral and oxidized states.

Table 1. Absorption Maxima[a] and Half-Wave Potentials[b] of **1**−**5**

	absorption maxima (nm)			potentials (V)	
	neutral	polaronic	π-dimeric	$E_{1/2}{}^1$	$E_{1/2}{}^2$
1	384	665, >1100	*c*	0.33	0.57
2	382	655, 1084	593, 948	0.33	0.83
3	409	730, >1100	663, 1062	0.23	0.71
4	382	658, 1094	598, 955	0.33	0.82
5	382	645, 1079	*c*	0.42	0.76

[a] Absorptions were measured in CH_2Cl_2 upon addition of oxidant Et_3OSbCl_6 at room temperature. [b] Half-wave potentials (all vs Fc/Fc^+) were measured in CH_2Cl_2 with 0.1 M $TBAPF_6$ as a supporting electrolyte under ambient conditions. [c] Not observed.

π-Dimer formation was further confirmed by EPR spectroscopy. EPR spectra were acquired for each of the CH_2Cl_2 solutions (0.2 mM for **1** and **2**, 0.4 mM for **5**) at room temperature. As expected, bis(radical cation) $\mathbf{1}^{2(\bullet+)}$ (Figure 3a, broken line) was EPR-active, showing a rather broad and featureless signal, which is very similar to that of radical cation $\mathbf{5}^{\bullet+}$ (dotted line). Note that $\mathbf{1}^{2(\bullet+)}$ consists of two independent radical cations. In contrast, $\mathbf{2}^{2(\bullet+)}$ (solid line) was almost EPR-silent, which indicates that the two radical cations are bound to form a π-dimer.

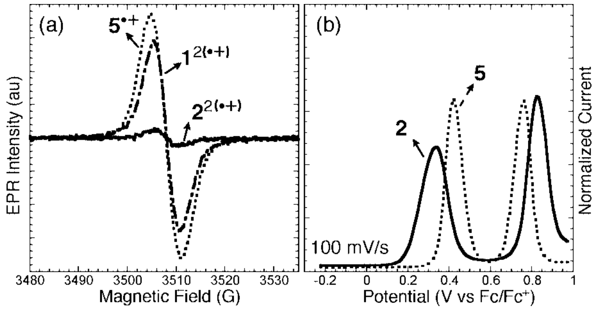

Figure 3. (a) 9-GHz EPR spectra of radical cations $\mathbf{1}^{2(\bullet+)}$ (broken line), $\mathbf{2}^{2(\bullet+)}$ (solid line), and $\mathbf{5}^{\bullet+}$ (dotted line) in CH_2Cl_2 at room temperature. (b) Differential pulse voltammograms of **2** (solid line) and **5** (dotted line) in CH_2Cl_2 (~0.5 mM) on a Pt button electrode with 0.1 M $TBAPF_6$ as a supporting electrolyte.

The evolution of the EPR signals of oxidized **2** and **5** was monitored as the oxidant (Et_3OSbCl_6 in CH_2Cl_2) was added

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(13) There is a possibility that the hydroxyl groups of **1** were alkylated by the Meerwein's salt. However, oxidation of **1** with a different oxidant ($FeCl_3$) resulted in the same absorption specta (Figure S2, Supporting Information).

(14) Shinkai, S. *Tetrahedron* **1993**, *49*, 8933–8968.

incrementally (Supporting Information). In the case of **5**, the signal increased gradually to a maximum. However, the initially developed signal for **2** decreased as more oxidant was added. This is in accord with what was observed by the UV−vis spectroscopy (Figure 2b); in **2**, radical cations appeared at the initial stages of oxidation, but the π-dimer dominated at higher oxidation levels.

The oxidation potentials of dimeric **2** and monomeric **5** were measured in CH_2Cl_2 solutions with 0.1 M $TBAPF_6$ as a supporting electrolyte under ambient conditions. In cyclic voltammetry, both **2** and **5** showed two 1-electron oxidation peaks, which correspond to radical cation(s) and dication(s), respectively (Table 1). However, the first oxidation of **2** took place at a potential lower than that of **5** (0.33 and 0.42 V, respectively, vs Fc/Fc^+), and the peak was broader. In contrast, the second oxidation of **2** was shifted to the higher potential. Differential pulse voltammetry (DPV, Figure 3b) reveals the differences more clearly. The first oxidation of the dimeric **2** occurred at a lower potential and the peak was broader, whereas the second oxidation was at higher potential when compared to that of the monomeric **5**. These data also are consistent with the π-dimer formation because an overpotential is required to oxidize the π-dimer, which is a stabilized species.

In conclusion, we have demonstrated that a stable π-dimer is formed upon oxidation of compounds **2**, **3**, and **4**, the model units of the proposed molecular actuator, in a solvent of low dielectric constant (CH_2Cl_2) at room temperature. Evidence from UV−vis, EPR, and DPV are all in agreement with the π-dimer formation. In addition, we found that π-dimer formation is dependent upon the conformational flexibility of the calix[4]arene hinge. We are currently seeking to produce polymeric actuating materials based upon these compounds.

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Supporting Information Available: Experimental details on the syntheses of **1**−**5**, UV−vis and EPR spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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