Stacking of oligo- and polythiophene cations in solution: Surface tension and dielectric saturation

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The stacking of positively charged (or doped) terthiophene oligomers and quaterthiophene polymers in solution is investigated applying a recently developed unified electrostatic and cavitation model for first-principles calculations in a continuum solvent. The thermodynamic and structural patterns of the dimerization are explored in different solvents, and the distinctive roles of polarity and surface tension are characterized and analyzed. Interestingly, we discover a saturation in the stabilization effect of the dielectric screening that takes place at rather small values of ϵ_0. Moreover, we address the interactions in trimers of terthiophene cations, with the aim of generalizing the results obtained for the dimers to the case of higher-order stacks and nanoaggregates. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2198811]

I. INTRODUCTION

The intermolecular interactions between conjugated polymers and oligomers in the condensed phase—whether in the solid state or in solution—entail a fundamental interest in the emerging field of molecular electronics, as they are decisive factors in the electronic and structural properties of these materials. The orientation and alignment of polymers in a solid matrix, the formation of aggregates in films and solution, or the ability of organic semiconductors to self-assemble, are the outcome of a complex balance between the spatial features of the molecules and the substrate and the interactions between them at the conditions of synthesis.[1–9] By dictating rules for aggregation, these interactions eventually shape properties such as charge delocalization and mobility[2,9–11] or optical[3,12–14] and electromechanical[15] responses.

Thiophene-derived oligomers and polymers represent today one of the most promising class of organic semiconductors, finding potential applications in a variety of electronic and electroactive devices.[16–18] Semiconducting properties arise with doping: therefore much of the basic research performed on these systems has addressed, in particular, the doped or oxidized species. Since the early 1990s electrochemical and spectroscopic evidences were gathered indicating that oxidized oligothiophenes reversibly associate in solution.[19–21] In a recent study,[22] we have outlined how this association is driven by three contributions: the attractive π-π interactions, the Coulombic repulsion, and the solvent effects. In the case of oligothiophene cations dimers, combination of half-filled highest occupied molecular orbitals (HOMOs) forms occupied bonding and empty antibonding orbitals, resulting in an interaction of covalent character, different in nature to the one arising in neutral dimers, of dispersive origin.[23] In vacuum, the electrostatic repulsion between the cations largely exceeds the covalent term,[22,24] making apparent the importance of the solvent (or of the counterions in the solid state case) in stabilizing the stacks. A polarizable dielectric medium favors concentration of charge in a small cavity, reverting the balance from net repulsion to attraction and stacking.

Continuum dielectric models have been successfully applied in structural and dynamical studies of conjugated polymers in organic solvents.[5,22] In the present paper, we employ a recently developed first-principles approach to describe the effect of a continuum solvent within the density-functional theory framework[25] and use it to explore the role of polarity and surface tension in the stabilization of dimers of polythiophene and oligothiophene radical cations. Furthermore, we examine the possibility of trimer formation as an intermediate step toward the nucleation of higher-order aggregates and to gain insight on self-assembly in solution. In charged dimers, at variance with the case of neutral dimers governed by van der Waals forces, interactions are predomi-

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nantly covalent and electrostatic, and density-functional theory (DFT) has proven to be sufficiently accurate when compared with highly correlated quantum-chemistry methods.[22] In our approach, the contribution of the surface tension to the solvation free energy is computed in a very natural fashion, as the product between the area of the cavity and the surface tension of the solvent.[25] This contribution is particularly important in dimerization processes, where the merging of two cavities into one provides an additional stabilizing term associated with the minimization of the total area of the cavity.

II. METHODOLOGY

All calculations in this work have been performed with the public domain Car-Parrinello parallel code included in the QUANTUM-ESPRESSO package,[26] based on density-functional theory, periodic-boundary conditions, and plane-wave basis sets. Vanderbilt ultrasoft pseudopotentials[27] have been used to represent the ion-electron interactions, in combination with the PBE approximation to the exchange-correlation term,[28] and with Kohn-Sham orbitals and charge density expanded in plane waves up to kinetic energy cutoffs of 25 and 200 Ry, respectively.

Solvation is described with a continuum model recently implemented by us in the QUANTUM-ESPRESSO package and described in detail in Ref. 25. In this approach, the solvent is represented as a dielectric medium surrounding a quantum-mechanical solute confined in a cavity delimited by an isosurface of electronic charge density. Adopting a common decomposition of the solvation free energy ΔG_{sol}, we have

$$\Delta G_{sol} = \Delta G_{el} + \Delta G_{cav} + \Delta G_{dis-rep}, \quad (1)$$

where ΔG_{el}, ΔG_{cav}, and $\Delta G_{dis-rep}$ are the electrostatic, the cavitation, and the dispersion-repulsion contributions, respectively.[29] In our implementation ΔG_{el} and ΔG_{cav} are considered explicitly, while $\Delta G_{dis-rep}$ is largely captured (by virtue of the parametrization) by the electrostatic term. In the following, we briefly review the approaches used to obtain ΔG_{el} and ΔG_{cav}.

The electrostatic interaction between the dielectric medium and the solute is calculated, as proposed by Fattebert and Gygi,[30,31] by solving the Poisson equation in the presence of a dielectric continuum with permittivity $\epsilon[\rho]$:

$$\nabla \cdot (\epsilon[\rho] \nabla \phi) = -4\pi\rho. \quad (2)$$

The function $\epsilon[\rho]$ is defined to asymptotically approach the permittivity of the bulk solvent ϵ_0 in regions of space where the electron density is low and to approach 1 in those regions where it is high.[25] In this way the dielectric medium and the electronic density respond self-consistently to each other through the dependence of ϵ on ρ and vice versa. The variation in the dielectric constant at the solvent-solute interface is controlled by two parameters ρ_0 and β, which determine the size of the cavity and the smoothness of the transition region. These are the only parameters entering the model, and our chosen values, $\rho_0 = 0.000\,78e$ and $\beta = 1.3$, represent a rather universal choice.[25] In particular, in the present case, we are interested not in the solvation energies themselves but in
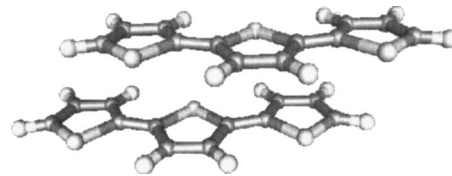

FIG. 1. A terthiophene dimer in the minimum energy configuration corresponding to the doubly charged state, in which one singly charged monomer is shifted 2.3 Å with respect to the other along the main axis.

their differences, which will have a weaker dependence on ρ_0.

The cavitation term is computed as the product between the surface tension of the solvent γ and the area of the cavity,

$$\Delta G_{cav} = \gamma S(\rho_0), \quad (3)$$

where $S(\rho_0)$ is the surface of the same cavity employed in the electrostatic part of the solvation energy and is defined by an isosurface of the charge density. This area can be easily and accurately calculated by integration in a real-space grid, as the volume of a thin film delimited between two charge density isosurfaces, divided by the thickness of this film. This idea has been originally proposed by Cococcioni et al.[32] to define a "quantum surface" in the context of extended electronic-enthalpy functionals:

$$S(\rho_0) = \int d\mathbf{r} \{\vartheta_{\rho_0-\Delta/2}[\rho(\mathbf{r})] - \vartheta_{\rho_0+\Delta/2}[\rho(\mathbf{r})]\} \times \frac{|\nabla\rho(\mathbf{r})|}{\Delta}. \quad (4)$$

The finite-difference parameter Δ determines the separation between two adjacent isosurfaces, one external and one internal, corresponding to density thresholds $\rho_0-\Delta/2$ and $\rho_0+\Delta/2$, respectively. The spatial distance between these two cavities—or the thickness of the film—is given at any point in space by the ratio $\Delta/|\nabla\rho|$. The (smoothed) step function ϑ is zero in regions of low electron density and approaches 1 otherwise, and it has been defined consistent with the dielectric function $\epsilon[\rho]$.

III. RESULTS AND DISCUSSION

Crystallographic data[33] and recent calculations[22,24] on oxidized dimers have indicated that the stacking of oligothiophene cations follows a "slipped" pattern where the layers are shifted along the molecular axis, as shown in Fig. 1. We have studied the dependence of the energy as a function of the lateral shift for oxidized terthiophene and polyquaterthiophene dimers in acetonitrile ($\epsilon_0 = 35.7$ and $\gamma = 28.7$ mN/m) at a fixed intradimer separation of 3.4 Å. In the calculations involving the terthiophene oligomers, Dirichlet boundary conditions in the electrostatic potential were applied, and the size of the unit cell was large enough to eliminate any significant interactions between the periodic images. In the case of the polymers, periodic-boundary conditions were used along the z axis (the molecular axis), keeping the Dirichlet boundary conditions in the other directions. The total charge of these systems is +2 (in the polymer, there is a positive charge every four thiophene rings). Our results are shown in Fig. 2: both the oligomer and the polymer ex-
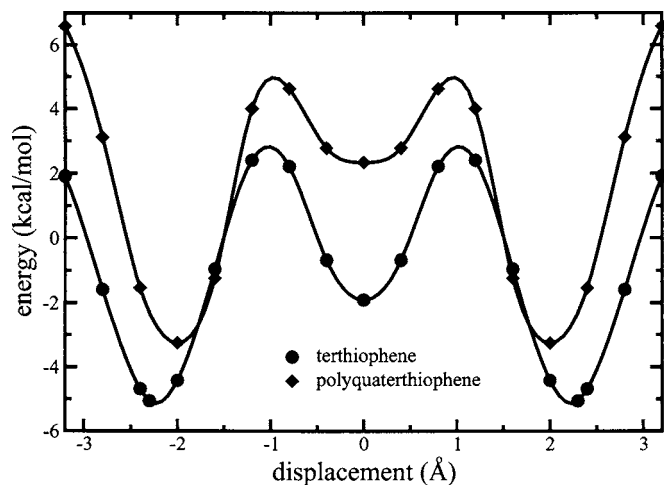
FIG. 2. Interaction energy as a function of the axial shift for the oxidized terthiophene and quaterthiophene dimers in acetonitrile.

FIG. 4. Interaction energy as a function of the interplanar separation between two singly charged terthiophene cations in water, acetonitrile, and dichloromethane.

hibit a similar pattern, with a global minimum at 2.3 Å for the terthiophene and 2.0 Å for the polyquaterthiophene. A local minimum at 0.0 Å (where the two layers are overlapping) is present in both cases. Interestingly, the net binding is very sensitive to the lateral shift, varying steeply in a range of 10 kcal/mol as one layer is slipped over the other. At shifts of about 1 Å off the minima, the π-π interaction between the cations appears clearly weakened, resulting in an unbound dimer.

The nature of the solvent does not have any significant effect on this characteristic pattern, even if it affects the magnitude of the interaction. This is shown in Fig. 3, where the terthiophene curve is displayed for three different media: acetonitrile, dichloromethane ($\epsilon_0=8.9$ and $\gamma=27.2$ mN/m), and water ($\epsilon_0=78.8$ and $\gamma=72.2$ mN/m). (We have chosen water as a case study given its distinctive polarity and surface tension, despite the low solubility exhibited by thiophene derivatives in this solvent.) Figure 4 explicitly illustrates the role of the solvent in the binding of the terthiophene cations, by showing the interaction energy as a

function of the intradimer distance at a fixed lateral shift of 2.3 Å. The binding energies are close to 5 kcal/mol for dichloromethane and acetonitrile and 12 kcal/mol in water (previous results using the Polarizable Continuum Model (PCM) and Gaussian basis sets to describe acetonitrile show a very good agreement with the present values[22]). These energies can be seen as a lower limit for the absolute value of the dimerization enthalpy ΔH_d, since the effect of the ionic environment was neglected in the calculations (the counterions in solution would differentially stabilize the doubly charged terthiophene dimer compared to two terthiophene cations; this effect has been recently discussed by Jakowski and Simons[34] for dimers of tetracyanoethylene anions $[\mathrm{TCNE}]_2^{2-}$). In fact, dimerization enthalpies between 7 and 14 kcal/mol have been reported for different terthiophene derivatives in apolar solvents.[35–37] The interplanar separations corresponding to the minima, in the range from 3.4 to 3.5 Å, are consistent with the distance of 3.47 Å obtained for substituted terthiophene cations in the solid state.[33] Figure 5 compares the potential energy surface of the oligo-
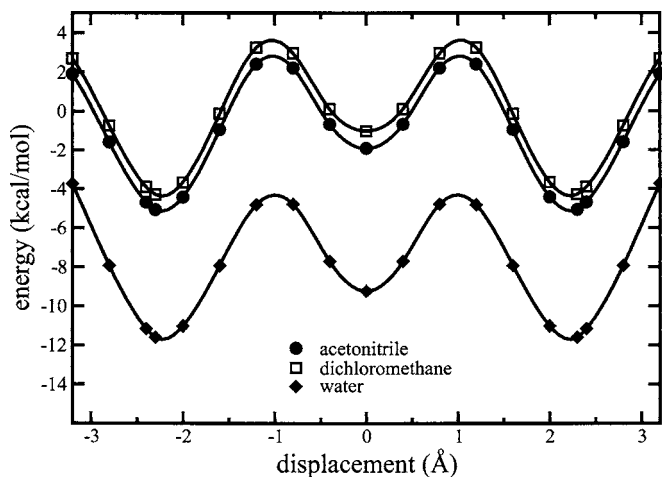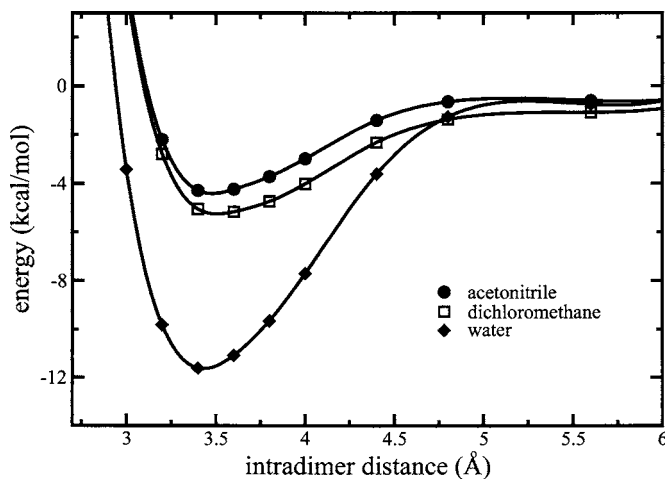

FIG. 3. Interaction energy as a function of the axial shift for the oxidized terthiophene dimer in water ($\epsilon_0=78.8$ and $\gamma=72.2$ mN/m), acetonitrile ($\epsilon_0=35.7$ and $\gamma=28.7$ mN/m), and dichloromethane ($\epsilon_0=8.9$ and $\gamma=27.2$ mN/m).
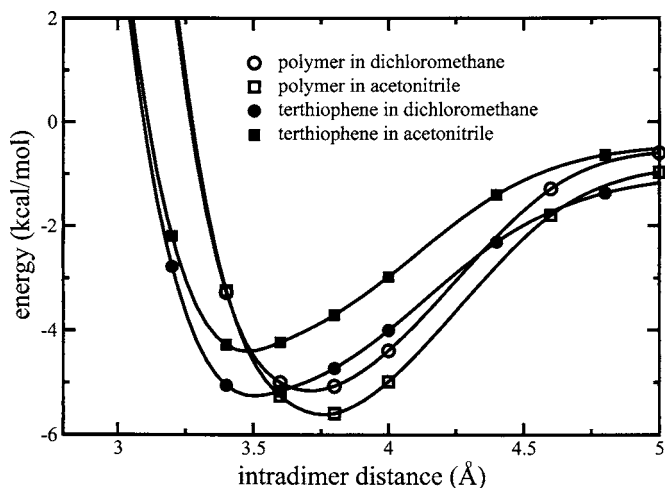

FIG. 5. Interaction energy as a function of the interplanar separation for the doubly charged dimers of polyquaterthiophene (open symbols) and terthiophene (closed symbols) in dichloromethane and acetonitrile.
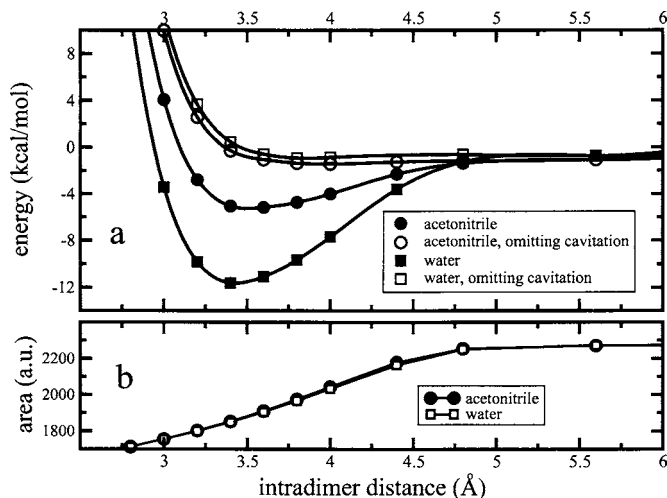
FIG. 6. (a) Interaction energy of two terthiophene cations in acetonitrile and in water, as a function of its separation. Open symbols curves were calculated omitting the cavitation contribution to the solvation energy, while the closed symbols curves include both the electrostatic and cavitation contributions. (b) Area of the solvation cavity as a function of the separation between the terthiophene cations. Beyond 4.75 Å the cavity splits in two, and the plotted area corresponds to two cavities containing one singly charged terthiophene each.
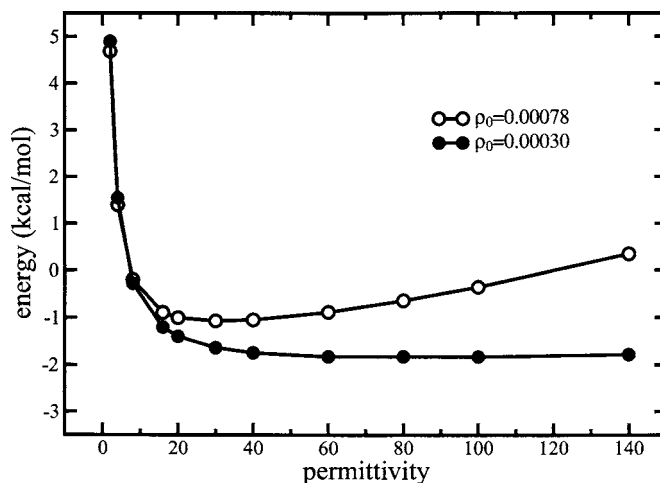

FIG. 7. Interaction energy between two terthiophene cations at a fixed separation as a function of the dielectric constant of the solvent, omitting the cavitation energy term, for two different thresholds ρ_0. The positive drift observed at high permittivity for $\rho_0 = 0.000\,78e$ is an artifact of the continuum model (see text).

mer with the one corresponding to the polymer (the latter was calculated at a fixed lateral shift of 2.0 Å). The equilibrium distance turns out to be around 0.3 Å larger in the periodic system, although it exhibits a slightly stronger binding. This is in agreement with experimental data showing that ΔH_d is enhanced by the length of the chain,[20] a trend related to a "dilution" of the Coulombic repulsion as the ratio between charge and oligomer size decreases.[22] At the same time, however, the increase in length at a given oxidation state would diminish the ratio between unpaired electrons available to π-π bonding and thiophene rings. Given these two opposite trends, the dilution of the repulsion and the decrease in the relative number of unpaired electrons, there should be a finite molecular length which maximizes the binding.[38]

The separate roles played by the dielectric screening of the solvent and its surface tension in the stabilization of the dimer are highlighted in Fig. 6. If the contribution of ΔG_{cav} was omitted, the binding curves would turn out to be very close to each other [Fig. 6(a)]. The larger γ in the case of water (72.2 mN/m vs 28.7 mN/m in acetonitrile) is responsible for the deeper minimum in the potential energy surface. The net effect of the surface tension is to minimize the area of the solvation cage, monitored in Fig. 6(b) as the cations are pulled apart. Beyond a separation of about 4.75 Å, the surface remains constant, indicating that the single cavity has split and each cation is enclosed in a separate cavity of area independent of the interplanar distance. In this situation there is no cavitation energy gain, and therefore the curves excluding and including ΔG_{cav} [open and closed symbols in Fig. 6(a), respectively] overlap on the right part of the plot.

The potential energy curves in Fig. 6(a) unveil an intriguing possibility: That the binding energy is not directly related to the dielectric constant of the solvent, as our intuition may suggest. This hypothesis is explored in Fig. 7,

where the interaction energy between two terthiophene cations separated by 3.6 Å is plotted as a function of the dielectric constant, ignoring the contribution of the surface tension. The results are somehow unexpected: A rather small increase in the permittivity with respect to the vacuum limit rapidly stabilizes the dimer, but once the dielectric constant is above 10 the effect of a further increase in polarity is very small. This behavior can be rationalized considering that a polarizable dielectric medium with low permittivity is already enough to screen most of the Coulombic repulsion between the two charges and to favor aggregation of these charges by polarizing itself. We note in passing that the positive drift observed at higher permittivities for the case of $\rho_0 = 0.000\,78e$ is an artifact of the continuum model. Since the dielectric constant is defined as a continuous function of the electron density, its value throughout the intradimer region may depart from 1, allowing the dielectric medium to fill some of the space between the cations and to interfere, though modestly, with the π-π bond. This effect will be enhanced at large values of ϵ_0 and ρ_0. In reality, instead, the solvent does not penetrate the intradimer space if the separation is 3.6 Å, regardless of ϵ_0. This spurious behavior is, in fact, absent in the curve computed with $\rho_0 = 0.0003$ in Fig. 7. What is remarkably captured by the continuum model is the saturation effects of polarity on the dimerization, occurring already for very low dielectric constants. These results are pretty much consistent with experimental observations that turn down a direct correlation between dimerization trends and polarity of the medium while emphasizing the dependence on solubility of the oligothiophenes.[39] To understand the effect of the solvent on ΔH_d, then one should consider other properties such as surface tension or specific interactions between the solute and the medium.

Are the thermodynamic and structural features found so far for the dimerization applicable to the stacking of multiple oligomer layers? It would be very interesting to know if or how the present results can be extended to processes such as aggregation and self-assembly in solution, involving the col-
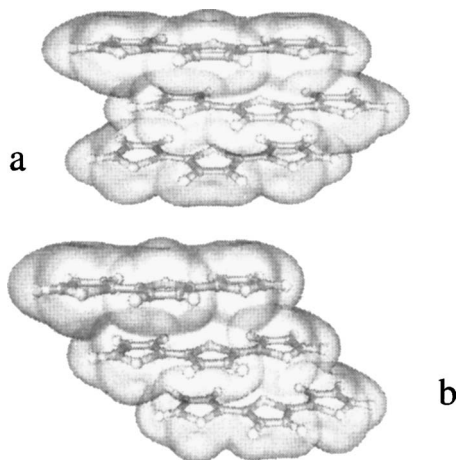
FIG. 8. Minimum energy structures for the terthiophene trimer in acetonitrile, surrounded by its corresponding solvation cavities defined by isosurfaces at $0.00078e$.

FIG. 10. Interaction energy as a function of the interplanar separation between three parallel terthiophene cations in acetonitrile. The top and the bottom layers are overlapping with each other, having an axial shift of 2.3 Å with respect to the central layer, as shown in Fig. 8(a).

lective pairing of many oligothiophene units. In an attempt to offer an answer, even if preliminary, to this question, we have studied the formation of trimers of terthiophene cations in acetonitrile. Figure 8 depicts the two configurations of minimum energy obtained for the trimer in acetonitrile, in which the third cation is shifted by ±2.3 Å with respect to the next oligomer. As shown in Fig. 9, where the interaction energy is plotted as a function of the lateral shift of the third cation, there is no significant energetic difference between these two minima. The curve corresponding to the dimer is plotted in the same figure: The pattern of valleys and peaks is preserved at the same lateral displacements when increasing the number of layers from 2 to 3. The differences in the relative depths of these curves can be ascribed to the fact that the same interplanar separation of 3.4 Å was adopted in the calculation of both, but the optimal separation in the trimer is longer, as can be seen in Fig. 10. This graph shows the interaction energy calculated for the trimer in acetonitrile as a function of the interplanar separation between layers (the interplanar separation between the first and the second layer is the same as that between the second and the third at each

point of the curve). For meaningful comparison with the dimer, depicted in the same graph, the energies were normalized to the number of π pairs, in this case, 2. Interestingly, the binding between two cations does not seem to be impaired by the presence of a third one: The interaction between stacks remains almost constant, even though the equilibrium distance increases in about 0.1 Å. This suggests that the energetic and structural results found for the cation dimers can be applied, to a large extent, to the case of more complex, larger aggregates consisting of multiple layers.

IV. SUMMARY

Our study has highlighted the separate roles of surface tension and the dielectric screening in the stabilization of charged thiophene oligomers and polymers stacks. The surface tension of the solvent is a driving force toward the minimization of the cavity area and therefore toward dimerization: There is an energetic payoff in accommodating two solutes in a single cavity of an area smaller than twice the one corresponding to the dissociated components. On the other hand, the dependence of the dimer stability on the polarity of the solvent alone is less evident. A dielectric effect is necessary to screen the electrostatic repulsion and to stabilize the charges in a small volume, but once the permittivity has reached a certain threshold, a further increase in polarity has a negligible contribution to the stabilization of the system. This observation is probably general to any π dimer of charged radicals—a hypothesis that could be interesting to test through explicit calculation.

The formation of trimers follows the same geometrical arrangement as the dimerization. A π bond on one of the oligomer planes does not seem to significantly affect the bond on the other. These results point to the conclusion that the organization of aggregates and stacks is governed by the same thermodynamics that is already manifested in the dimerization.
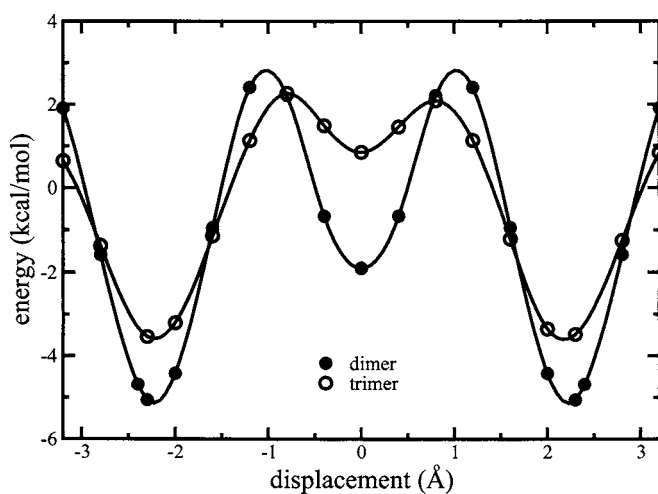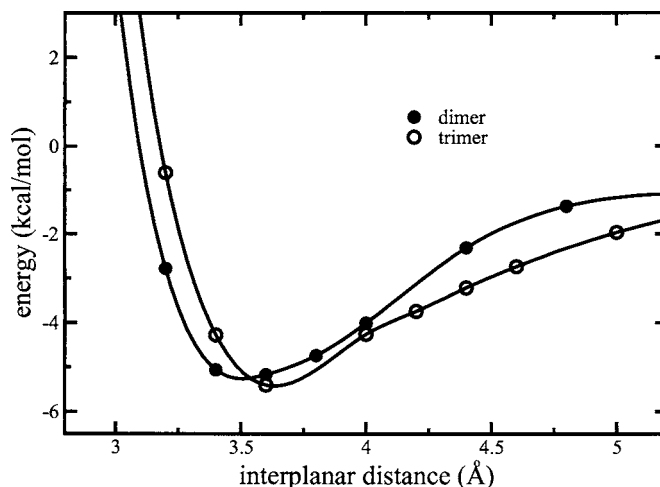

FIG. 9. Interaction energy as a function of the axial shift between a doubly charged terthiophene dimer and a third terthiophene cation in acetonitrile.

ACKNOWLEDGMENTS

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