Charged Push−Pull Polyenes in Solution: Anomalous Solvatochromism and Nonlinear Optical Properties

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Received: December 9, 2002; In Final Form: May 22, 2003

The linear and nonlinear optical properties of charged push−pull polyenes (CPPP) are, respectively, of interest in connection with unusual linear spectroscopic solvatochromic behavior in solution and other polar media and applications ranging from second harmonic generation to imaging and probing of biological systems. The CPPP are charged conjugated quasi-one-dimensional molecules containing an electron-donating group (D) and an electron-acceptor group (A) interacting via a π-conjugated bridge. Here we present a theoretical description for photoinduced charge transfer for such molecules in solution, based on a two valence bond state electronic description together with inclusion of a geometrical coordinate for the bridge and a solvent coordinate describing nonequilibrium solvation of the molecule. The theory both accounts for the anomalous linear solvatochromic behavior and provides a treatment of CPPP nonlinear optical properties in solution.

1. Introduction

In this paper, we develop a theoretical description for photoinduced charge transfer (CT) for the important molecular class of charged push−pull polyene molecules (which are also called hemicyanines) in polar environments. Hereafter, we designate such charged push−pull molecules via the notation CPPP. The so-called "push−pull" compounds are conjugated quasi-one-dimensional molecules containing an electron-donating group (D) and an electron-withdrawing group (A) interacting via a π-conjugated system (cc). A charged example is shown in Figure 1 and is in contrast to the "normal" or noncharged push−pull polyenes, which we will designate by PPP, illustrated in Figure 2.

By the photoinduced CT terminology used above, we mean a CT that is induced by optical excitation such that the charge distribution of the Franck−Condon accessed electronic excited state differs significantly from that in the ground electronic state. In the most primitive and limited picture, there is a CT from the donor to the acceptor group in the electronic transition. This photoinduced CT is to be distinguished from the situation where after excitation a subsequent chemical reaction occurs, as in, for example, photoisomerization, twisted intramolecular charge transfer, or excited-state proton transfer.[1]

The photoinduced CT for the CPPP and the PPP families is central for two extensively studied experimental contexts: (a) their linear spectroscopy, that is, absorption and fluorescence, and the influence of the environment thereupon; (b) their nonlinear optical properties in polar environments. We now give an overview of these contexts, beginning with the second.

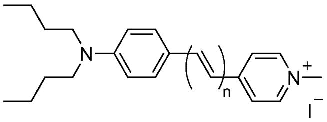

Figure 1. Example of charged push−pull polyene.

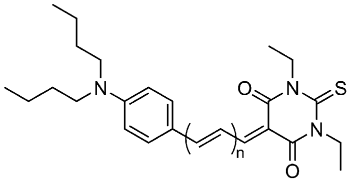

Figure 2. Example of "normal" push−pull polyene.

Molecular nonlinear optics[2] (NLO) has attracted major attention for the past two decades, in large part owing to its applications in various fields, including telecommunications, optical data storage and optical information processing,[3] optical power limitation,[4] microfabrication, and optical imaging of biological media.[5] Considerable experimental and theoretical work has been dedicated to the design of molecules with optimized NLO responses.[6,7] The linear and nonlinear optical properties of such compounds can be significantly influenced by the polarity of their environment.[8,9] This feature certainly must be taken into account, because most potential applications involve condensed media, in which local electric fields can significantly influence the molecular NLO responses. Accordingly, significant effort has been devoted to the investigation of electric local field and polarity effects on optical linear and nonlinear responses of push−pull dipolar compounds.[10−17]

Most such efforts have focused, however, on *neutral* dipolar molecules. For a different molecular class, *charged* cationic push−pull chromophores, such as stilbazolium derivatives,[18] have been shown to have very large NLO responses in condensed media and are particularly promising for assorted

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10.1021/jp0276597 CCC: $25.00

applications, ranging from second-harmonic generation and electrooptical materials[19] to high-resolution imaging of biological cells.[20] Amphiphilic styryl dye derivatives have been used, for example, for imaging of biological processes such as fusion and adhesion[21] and are particularly promising as voltage-sensitive probes for real-time in vivo monitoring of cellular membrane electric potentials.[22−24] These two uses are at the heart of the design of neuroelectronic devices, coupling neurons and silicon chips.[25]

The optical properties of such charged push−pull chromophores are known experimentally to be responsive to the environment and local electric fields.[26,27] In fact, the spectroscopic behavior of hemicyanine dyes (e.g., Figure 1) with increasing solvent polarity is quite unusual: the absorption spectrum is blue-shifted, while the fluorescence spectrum is red-shifted, that is, the absorption energy increases, while the emission energy decreases.[26−30] We emphasize that such behavior is doubly unusual. First, the absorption and fluorescence spectra shift in *opposite* directions; second, a more polar solvent shifts the absorption spectrum to the *blue*. As discussed in detail in section 2, such opposite shifts of absorption and fluorescence spectra are unexpected for absorption and emission processes involving the same excited electronic state. In the simple (and common) view in which one only considers the equilibrium solvation of the ground and excited states, the solvent polarity shifts of the absorption and fluorescence would be in the same direction. In addition, the observed blue shift in absorption is rather uncommon for push−pull polyenes.

There have been some previous attempts to explain aspects of these anomalies, but they are too restrictive, focusing solely on the absorption blue shift, and unfortunately are incorrect because when extended to the emission behavior, these explanations predict a blue shift, in contradiction with experiment.[26,32,33]

In what follows, we focus on both the explanation of the above-described unusual spectroscopic behavior and the treatment of the NLO properties of the CPPP molecular class of chromophores. These are, in fact, intimately connected: a correct treatment of the absorption and its solvatochromism is required to account for the NLO properties and their environmental sensitivity.

To this end, we employ and extend the basic formulation of the previous theoretical work of Thompson et al.,[16,17] which is couched within the fundamental framework of a two valence bond (VB) state description[14,16,17,34−37] and includes explicitly both the influence of nonequilibrium solvation—required by the Franck−Condon nature of the spectroscopic transitions—and the geometrical coordinate associated with a change in single and double bond alternation for the ground and excited states. The two VB state formulation for polyenic systems was introduced in different ways by the Goddard group[14] and by Barzoukas and Blanchard-Desce and their collaborators.[34,38−40] The simultaneous inclusion of the geometric bond alternation coordinate and a nonequilibrium solvation coordinate in the two VB state formulation of Barzoukas and Blanchard-Desce was first accomplished in refs 16, 17, and 41.

The two VB state formulation is particularly useful for the discussion of NLO properties because NLO responses have their fundamental origin in the feature that the ground and excited (adiabatic) electronic states are *mixtures* of the (diabatic) VB states, the latter being strongly electronically coupled. This essential point can be illustrated by consideration of the (linear) polarizability α. This will be largest when the ground electronic state is close to an equal mixture of the VB states; the molecule is then easily polarizable over these states. Further, it is the feature that this degree of ground state mixing can be *altered*—by different donor and acceptor groups, intervening chains, and solvent environments—that needs to be comprehended and exploited by molecular engineering and choice of environment to optimize the NLO properties.

This strongly electronically coupled two VB state perspective has not been much employed in the discussion of spectroscopic properties, but as will be seen, it provides both a natural, convenient, and illuminating description of the spectroscopy and a direct connection to NLO properties.

Our major focus will be on the CPPP molecule in a polar environment in the *absence* of any counterion. However, our analysis in the general case for both normal and charged polyenes is valid for the charged polyene together with its counterion; we only neglect the counterion when applying the general model in specific model applications within. We also justify the neglect of the counterion. We shall see, for example, that the anomalous spectroscopic behavior can already be predicted without any influence of a counterion.

After the work presented here was completed, we became aware of the work of Fromherz,[42] in which a correct qualitative explanation of the anomalous spectral shifts was given. As described in more detail within, the present work goes considerably beyond the Fromherz analysis in its generality and predictions. Thus, for example, our treatment is able to account for the fact that these anomalous shifts will not always be observed for CPPP. Further, a considerable portion of the theoretical description is sufficiently general that it can provide a starting point for the modeling of the linear and nonlinear optical properties of polyenes in complex media such as membranes. In addition, our analysis is couched directly in terms of a two electronic level, two VB state formulation—involving strong electronic coupling between the VB states[14,34,39]—which allows a simple and direct discussion of the NLO properties, which have not been previously treated.

We make several explicit restrictions in our development. The first is that, as noted above, we are here only concerned with photoinduced CT and related matters and not with any excited electronic state reaction.[43] The second is that the polyene electronic structure should be satisfactorily described in terms of two VB components, which is evidently not always the case.[44]

The outline of the remainder of this paper is as follows. In section 2, we present a qualitative analysis intended to clarify the basic issues for the spectroscopic anomalies in the traditional view, the difficulties with that view for the CPPP, and the correct qualitative description, which is explicitly constructed in the remainder of the paper. The theoretical formulation is constructed in section 3, in which the general equations necessary for analysis of the solvent polarity influence on the spectroscopic transitions are derived. Section 4 concerns the analysis of the conditions necessary for the observation of anomalous solvatochromism and focuses attention on the validity of the traditional point dipole view for the chromophoric molecule, as well as the influence of the molecular size and the donor and acceptor group separation. In section 5, we specialize to a particular model, involving a Marcus−Born description of various solvation terms, to make explicit the conclusions of the preceding sections. Section 6 discusses the CPPP NLO properties and their contrast with those for PPP. Summarizing remarks are given in section 7.

2. Qualitative Analysis

2.1. Traditional Picture. *2.1.1. Traditional Picture for Normal Polyenes.* Push−pull polyenes can be described by two

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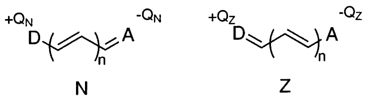

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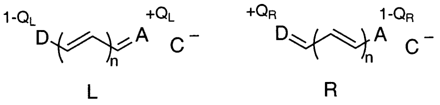


resonance valence-bond (VB) states of fixed charge and geometric character: the neutral (N) and zwitterionic (Z) forms (see Scheme 1). In the neutral state, the charge transfer between the two endgroups is very limited, and the charges $\pm Q_N$ remain small; by contrast, in the zwitterionic state, the charge separation is significant, resulting in charges $\pm Q_Z$ on the endgroups. In addition, the sequence of single and double bonds in the polyenic bridge is reversed in the two VB states, as is required by the different charge distributions.

For simplicity, in the qualitative discussion that follows, we use a primitive electronically diabatic perspective: the ground state is identified as the lower state among the N and Z states (usually the N state), while the excited state is identified as the other VB state (usually the Z state).

In the extremely well-known traditional picture,[45] the solvatochromic behavior of a molecule in solution can be predicted by the comparison of its dipole moments in the electronic ground and excited states, μ_g and μ_{ex}, respectively. If the excited state exhibits a larger dipole moment than the ground state, it is preferentially stabilized by the solvent and the energy gap between the two states decreases if the solvent polarity increases, that is, the absorption and emission spectra both shift to the red. Conversely, if the ground state is more polar than the excited state, a more polar solvent shifts the absorption and emission spectra to the blue. With this traditional approach, when the *same* excited state is involved, absorption and emission wavelengths always shift in the same direction when the solvent polarity changes. (We will only use this primitive description in this section.)

2.1.2. Failure of the Traditional Picture for Charged Polyenes. While normal PPP are globally neutral and do not bear any net charge, in cationic push−pull polyenes, a positive charge is present on the polyene and balanced by a counterion. The latter can be either free or attached to the acceptor endgroup by a nonconjugated bridge, typically an alkyl chain.[26] For these CPPP molecules, we will again use two VB states, but this time they bear a positive unit net charge, located either mainly on the acceptor group (state L) or mainly on the donor group (state R) (Scheme 2). Again, the bonding pattern of the conjugated chain is reversed between the two VB states.

We can again first apply the standard point dipole approach to predict the spectral behavior with increasing solvent polarity. In the ground state, the polyene positive charge is mainly located on the acceptor group, and at equilibrium, the counterion C^- is nearby: DccA$^+$ C^-. The ground-state dipole moment is due to the charges on A and C and, because of the proximity of the two groups, is quite small. On the other hand, in the excited state, the positive charge is mainly located on the donor endgroup, and just after the optical transition, the counterion has yet not moved and is still close to the acceptor: $^+$DccA C^-. The excited-state dipole moment is thus much larger because the charges are far apart. In the standard picture, we should thus have the case of a weakly polar ground state with a highly polar excited state. A more polar solvent should therefore shift both the absorption and emission spectra to the red. If the counterion is ignored, DccA$^+$ → $^+$DccA, the conclusion of the argument is not clear, because the relative "polarity" or degree of interaction with the solvent of the ground- and excited-state charge distributions is perhaps no longer obvious. Nonetheless, in the standard view in which one only considers the equilibrium solvation of the ground and excited states, the absorption and fluorescence solvent polarity shifts would be in the same direction.

And yet, experimentally, when the solvent polarity is increased, if the emission wavelength indeed shifts to the red, the absorption wavelength shifts to the blue.[26,32,33,42] The traditional picture cannot explain this behavior. First, it predicts that absorption and emission spectra always shift in the same direction, provided that the excited state involved is the same. In addition, the absorption blue shift is only predicted when the ground state is more polar than the excited state, which is rather uncommon for push−pull polyenes but occurs in some well-known cases such as MOED and polar merocyanines.[31] For the CPPP, if the counterion is included, the image DccA$^+$ C^- → $^+$DccA C^- for the absorption depicts a large dipole moment increase and thus a red shift with increasing solvent polarity. If the counterion is neglected, the direction of the absorption solvent shift will depend on the relevant relative stabilization of $^+$DccA versus DccA$^+$.

Thus we have to (and will) explain two essential points: (a) the fundamental origin of the anomalous behavior and (b) why the traditional picture fails to predict that behavior.

2.2. Correct Qualitative Description. The rigorous development of the theoretical formalism to explain the CPPP anomalous solvatochromism requires a detailed analysis and will be presented in later sections. Here we present the key ideas, in a simple context, that form the basis of that rigorous development.

We study the solvatochromism of a CPPP of which the electron-accepting and electron-donating groups A and D have the same size, and we ignore the counterion (this picture is therefore relevant only for polar solvents, in which the electrostatic interaction between the cationic polyene and the counterion is screened by the solvent and in which there is no aggregation of the charged polyene molecules). We also ignore the issue of internal geometric rearrangements in the transitions. In our discussion, we will shift the description from the electronically *diabatic* VB description—in which those VB states are uncoupled—to the electronically *adiabatic* one, in which the adiabatic ground and excited states are different combinations of the VB states. These mixtures arise from the electronic coupling between the VB states, which is quite large (∼1 eV[14,34,39]) and cannot be ignored.

Upon excitation from the electronic ground state to the excited state, a CT occurs from one endgroup to the other. Therefore, the solvent configuration, which was in equilibrium with the charge distribution of the ground-state molecule, is out of equilibrium with the new charge distribution of the Franck−Condon excited state. Hence, the absorption transition energy is the *sum* of two contributions, as illustrated in Figure 3: the first is the energy gap between the equilibrated adiabatic ground and excited states V_{eq}^{adia}; the second is the (adiabatic) solvent reorganization energy in the excited state Λ_s^{ex}, that is, the difference between the nonequilibrium (nuclear) solvation free energy of the excited-state evaluated in the ground-state equilibrium solvent configuration and in the excited-state equilibrium solvent configuration.

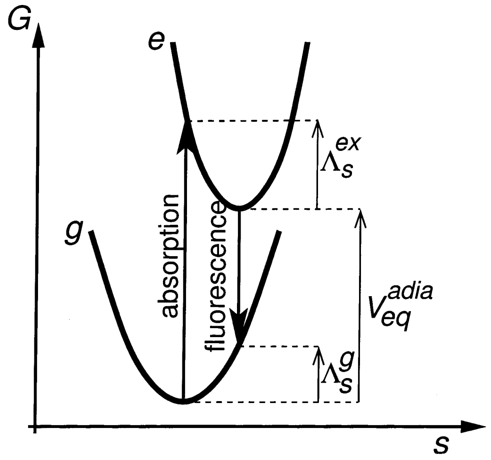


Figure 3. Schematic picture of the electronically adiabatic ground- and excited-state free energy surfaces in the solvent coordinate. The energy gap, $V_{\mathrm{eq}}^{\mathrm{adia}}$, between the equilibrated adiabatic ground and excited states and the solvent reorganization energies in the adiabatic ground and excited states, $\Lambda_{\mathrm{s}}^{\mathrm{g}}$ and $\Lambda_{\mathrm{s}}^{\mathrm{ex}}$, are indicated.

Similarly, for fluorescence, the emission transition energy is the *difference* between the adiabatic equilibrium energy gap $V_{\mathrm{eq}}^{\mathrm{adia}}$ and the solvent reorganization energy, but this time in the adiabatic ground state, $\Lambda_{\mathrm{s}}^{\mathrm{g}}$.

$$E_{\mathrm{abs}} = V_{\mathrm{eq}}^{\mathrm{adia}} + \Lambda_{\mathrm{s}}^{\mathrm{ex}}; \quad E_{\mathrm{em}} = V_{\mathrm{eq}}^{\mathrm{adia}} - \Lambda_{\mathrm{s}}^{\mathrm{g}} \qquad (1)$$

To elucidate the solvent polarity influence on the absorption and emission transition energies, we first focus on how the adiabatic equilibrium energy gap and the adiabatic solvent reorganization energies are affected by a solvent polarity increase. In the present illustrative case, the two endgroups have identical sizes. Hence, whether the positive charge is on one endgroup or the other, the electrostatic interaction energy with the solvent is the same, and a more polar solvent solvates in a similar manner the ground and excited states. Thus, to zeroth order, we can assume $V_{\mathrm{eq}}^{\mathrm{adia}}$ does not change with solvent polarity.

On the other hand, when the solvent polarity increases, the solvent reorganization energy increases, both in the ground and in the excited states. This follows from the feature that the reorganization free energies measure the free energy difference for a given state created in a nonequilibrium environment compared to that in its equilibrium environment.

Thus when the solvent polarity is increased, $V_{\mathrm{eq}}^{\mathrm{adia}}$ remains nearly unchanged, whereas both $\Lambda_{\mathrm{s}}^{\mathrm{g}}$ and $\Lambda_{\mathrm{s}}^{\mathrm{ex}}$ increase. From eq 1, we immediately see that this implies that the absorption energy increases while the emission energy decreases, that is, the absorption spectrum exhibits a blue shift and the fluorescence spectrum a red shift. Thus, the peculiarity of those so-called anomalous spectral shifts follows naturally; it does not lie in the presence of the counterion.

If we now turn to endgroups with different sizes, the electrostatic interaction energy with the solvent is different in the ground and excited states: a more polar solvent preferentially solvates one adiabatic state. Hence, in this case, increasing the solvent polarity changes the adiabatic equilibrium gap $V_{\mathrm{eq}}^{\mathrm{adia}}$, which affects the absorption and emission transition energies in the same direction (see eq 1). The effect originating from the different sizes of the two endgroups modulates the magnitude of the absorption blue shift and the fluorescence red shift found previously and, if large enough, can even change the direction of those shifts.

Through this very qualitative approach, we have highlighted the twofold role of the solvent polarity. First, a more polar solvent increases the solvent reorganization energy, both in the ground and in the excited states, and this tends to increase the Stokes shift, defined as the difference between the absorption and emission energies $E_{\mathrm{abs}} - E_{\mathrm{em}}$; second, a more polar solvent also affects the energy gap between the equilibrated adiabatic ground and excited states, and that tends to shift both the absorption and fluorescence spectra in the same direction, while keeping the Stokes shift equal. In normal polyenes, the latter effect is predominant and a more polar solvent shifts both the absorption and emission spectra in the same direction. But in contrast, for CPPP, in the most common case, the first effect is predominant and that results in a blue shift in absorption and a red shift in emission with increasing solvent polarity.[46]

2.3. Comparison with the Fromherz Approach.

As noted in the Introduction, the blue shift in absorption and red shift in emission with increasing solvent polarity for charged push−pull polyenes have already been interpreted by Fromherz.[42] Here, we briefly discuss his approach and indicate how the present treatment goes beyond it.

Fromherz begins by ignoring the counterion for the CPPP, which in any event could not be readily incorporated in his model. He observes that the sum of the absorption and emission energies, $E_{\mathrm{abs}} + E_{\mathrm{em}}$, is approximately constant for several hemicyanine dyes (charged push−pull polyenes) and over a wide range of solvent polarity. He concludes that the solvation energies of the ground and excited states are similar and that their charge distributions are reversed. Fromherz models the charge distribution as sums of a point charge plus a point dipole, which are mirror images in the ground and excited states.

Starting from this description, he correctly accounts for the anomalous solvatochromism, assigning the blue shift to the enhancement of a solvent reorganization energy with increasing solvent polarity and the fluorescence red shift to the same type of effect for the excited-state emission. These shifts were successfully formalized within a Marcus−Born model.

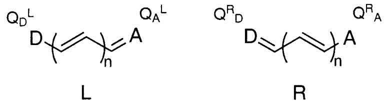
We consider that Fromherz's qualitative interpretation of the spectral behavior is surely correct and that that work represents a significant pioneering contribution. However, there are some important limitations of the basic model and, more significantly, of the formulation of the problem, which the present treatment removes, as now discussed.

In the Fromherz model, a single spherical cavity for the whole polyene is used; this cannot properly describe polyenes with long bridges between the donor and acceptor moieties, for which each endgroup should be embedded in its own cavity. Our formulation is not so limited and can, for example, accommodate two distinct cavities. In this manner, the two donor and acceptor endgroups can be surrounded by media with different dielectric constants, and this could be used for a (very simplified) description of this type of molecule inserted in a biological membrane, as is the case when this molecule is used to probe the cellular potential.[20,22] Stated generally, the present formulation is sufficiently general to open the way for applications to modeling of CPPP in biological membranes.

Further, the change in the bond length pattern along the chain between the ground and excited states is not taken into account; in our formulation, this inclusion has the important effect of providing an additional reorganization energy beyond that of the solvent.

In the Fromherz formulation, a key role is played by the constancy of the sum of the absorption and emission energies, $E_{\mathrm{abs}} + E_{\mathrm{em}}$, of charged polyenes over a range of molecules and

SCHEME 3



solvent polarities. This is however too restrictive and not generally correct. For example, the CPPP rhodamine 700 exhibits a red shift both in absorption[47] and in emission for increasing solvent polarity. Further, the formulation does not give the conditions that have to be fulfilled for the anomalous behavior to be observed, a feature provided by the present formulation.

But perhaps most importantly, the Fromherz formulation assumes that there are fixed charge distributions for the ground and excited states with no possibility of describing their changes in different environments. By contrast, the present formulation, expressed in terms of electronically coupled VB states to generate the electronically adiabatic ground and excited states, automatically accounts for shifting electronic structures of the chromophore, an effect that is critical for the description of CPPP nonlinear optical properties.

3. Theoretical Formulation

3.1. Two VB State Description. We now give a rigorous development of the qualitative picture sketched above and build a general analytic model, both for CPPP and for PPP molecules.

To construct a general model describing both the normal (globally neutral) and charged push−pull polyenes, we use the two VB states in Scheme 3, labeled L and R for left and right, respectively, where the charges on the endgroups are independent.

In the CPPP case, we neglect the counterion. We have already shown qualitatively in section 2.2 that the counterion is not necessary to explain the solvatochromic behavior; further, with polyenes in which the counterion is attached via a nonconjugated chain of variable length, it is experimentally observed[26] that the counterion has very little effect on the absorption energy.[48]

The nonequilibrium solvation of normal push−pull polyenes has already been studied within the framework of such a two VB state model in ref 16, and our formulation here will proceed along the same lines. We consider two coordinates: a geometric one, q, to account for the single/double bonding pattern reversal and a solvent coordinate, s, measuring the slow nuclear polarization of the solvent. The fast electronic polarization is considered to be always equilibrated. Both coordinates are supposed to be harmonic, and the free energies of the two VB states are (see Figure 4)

$$G^{L}(q,s) = G_{s}^{L} + \lambda_{s}\left(\frac{s - s_{0}^{L}}{s_{0}^{R} - s_{0}^{L}}\right)^{2} + \lambda_{q}\left(\frac{q - q_{0}^{L}}{q_{0}^{R} - q_{0}^{L}}\right)^{2}$$

$$G^{R}(q,s) = V_{0} + G_{s}^{R} + \lambda_{s}\left(\frac{s - s_{0}^{R}}{s_{0}^{L} - s_{0}^{R}}\right)^{2} + \lambda_{q}\left(\frac{q - q_{0}^{R}}{q_{0}^{L} - q_{0}^{R}}\right)^{2} \quad (2)$$

We focus first on quantities associated with the two diabatic VB states. The free energies are referenced to the gas-phase free energy of the L state. V_0 is the gas-phase energy gap between the equilibrated VB states; $G_{s}^{L}(\epsilon)$ and $G_{s}^{R}(\epsilon)$ are the respective equilibrium solvation free energies of the VB states when both the electronic and orientational polarizations of the solvent are equilibrated; ϵ is the static dielectric constant of the solvent; $s_{0}^{L,R}$ and $q_{0}^{L,R}$ are the equilibrium values of the solvent and geometric coordinates in the L and R VB states. λ_s and λ_q are the geometric and solvent reorganization energies, which are supposed to be the same for both VB states. Similarly to λ_s, λ_q measures a certain nonequilibrium−equilibrium energy difference due to the geometrical coordinate; if, for example, the R state in Scheme 3 is created at the geometry of the L state, its geometry will relax to its proper one, the energy change involved being λ_q. The solvent reorganization energies and the equilibrium solvation energies depend on the solvent polarity, in a fashion made explicit later.

Those two (diabatic) VB states are strongly electronically coupled, resulting in the electronically adiabatic ground and excited states. Thus, the ground- and excited-state wave functions, Ψ_g and Ψ_e, are mixtures of the two VB configurations, ψ_L and ψ_R, and can be expressed as[34]

$$\Psi_{g,ex} = \sqrt{\frac{1 - \mathrm{MIX}_{eq}^{g,ex}}{2}}\,\psi_{L} + \sqrt{\frac{1 + \mathrm{MIX}_{eq}^{g,ex}}{2}}\,\psi_{R} \quad (3)$$

The MIX_{eq}^{g} and MIX_{eq}^{ex} parameters measure the relative proportions of the two VB states in the equilibrated ground and excited states, respectively; their values range from -1, where the considered adiabatic state corresponds to the pure L diabatic state, to $+1$, where the adiabatic state is the pure R diabatic state.

The adiabatic ground- and excited-state free energies are given by

$$G^{g,ex}(q,s) = \frac{G^{L}(q,s) + G^{R}(q,s)}{2} \mp \frac{1}{2}\sqrt{(G^{R}(q,s) - G^{L}(q,s))^{2} + 4t^{2}} \quad (4)$$

where t is the electronic coupling between the two VB states. The coupling for push−pull molecules is inferred to be large in the 1 eV range.[14,34,39] Such a large value for the coupling highlights the important point that the two VB state description is only an effective description. Thinking in terms of two uncoupled VB states is attractive because it gives a useful insight into the behavior of those molecules, for example, their nonlinear optical properties. Yet those two VB states then have to be mixed with a self-consistently determined electronic coupling to produce the required properties of the electronically adiabatic ground and first excited states, which turn out to be quite far from the pure VB states because of the large electronic coupling.

The energy gap between the *adiabatic* ground and excited-state surfaces in a given configuration (q,s) is related to the energy gap between the *diabatic* states in the same configuration, $V_{dia}(q,s) = G^{R}(q,s) - G^{L}(q,s)$

$$G^{ex}(q,s) - G^{g}(q,s) = \sqrt{(V_{dia}(q,s))^{2} + 4t^{2}} \quad (5)$$

The absorption and emission transition energies are therefore directly related to the diabatic energy gap in the global minimum of the energy surfaces of the adiabatic ground and excited states, respectively.

In these global minima, both the molecular geometry and the solvent orientational polarization are at equilibrium. The ground-state equilibrium values of the geometric and solvent coordinates, noted q_{eq}^{g} and s_{eq}^{g}, are found by the conditions $\partial G^{g}/\partial s = \partial G^{g}/\partial q = 0$. Similarly, for the adiabatic excited state, the global minimum position satisfies $\partial G^{ex}/\partial s = \partial G^{ex}/\partial q = 0$. The resulting

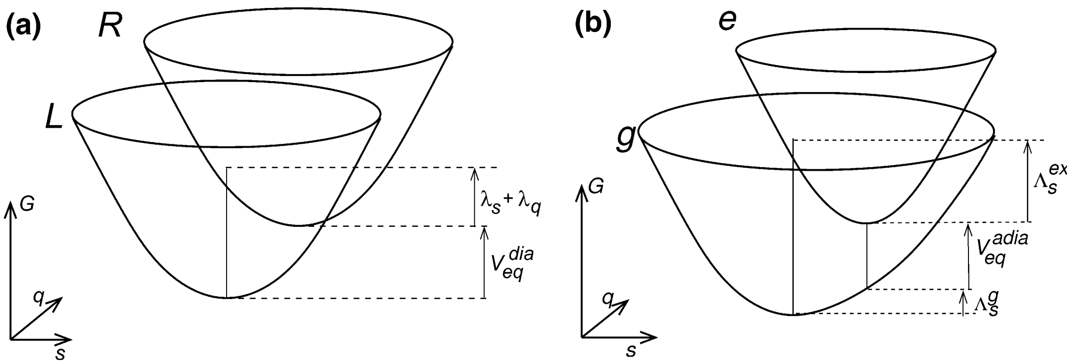


Figure 4. Schematic pictures along the solvent (s) and geometric (q) coordinates of (a) the diabatic free energy surfaces, where the diabatic equilibrium free energy gap, $V_{\mathrm{eq}}^{\mathrm{dia}}$, and the total diabatic reorganization energy, $\lambda_{\mathrm{s}} + \lambda_{\mathrm{q}}$, are indicated and (b) the resulting adiabatic ground and excited electronic free energy surfaces, where the adiabatic equilibrium free energy gap, $V_{\mathrm{eq}}^{\mathrm{adia}}$, and the adiabatic reorganization energies in the ground and excited states, $\Lambda^{\mathrm{g,ex}}$ are indicated.

geometric and solvent equilibrium coordinates for the ground and excited states are[16]

$$q_{\mathrm{eq}}^{\mathrm{g,ex}} = \frac{q_0^{\mathrm{L}} + q_0^{\mathrm{R}}}{2} + \frac{q_0^{\mathrm{R}} - q_0^{\mathrm{L}}}{2}\mathrm{MIX}^{\mathrm{g,ex}}(q_{\mathrm{eq}}^{\mathrm{g,ex}}, s_{\mathrm{eq}}^{\mathrm{g,ex}})$$
$$s_{\mathrm{eq}}^{\mathrm{g,ex}} = \frac{s_0^{\mathrm{L}} + s_0^{\mathrm{R}}}{2} + \frac{s_0^{\mathrm{R}} - s_0^{\mathrm{L}}}{2}\mathrm{MIX}^{\mathrm{g,ex}}(q_{\mathrm{eq}}^{\mathrm{g,ex}}, s_{\mathrm{eq}}^{\mathrm{g,ex}}) \qquad (6)$$

We have adopted the convention in which we keep the same meaning for the MIX parameter, both in the adiabatic ground and excited states: MIX = −1 always designates an adiabatic state that is the pure L state, and MIX = +1 corresponds to a pure R state. Note however that the equilibrium value of MIX in the excited state is different from what it is in the ground state.[50]

From the locations of the minima on the adiabatic ground- and excited-state surfaces, eq 6, the absorption and emission transition energies are

$$E_{\mathrm{abs,em}} = G^{\mathrm{ex}}(q_{\mathrm{eq}}^{\mathrm{g,ex}}, s_{\mathrm{eq}}^{\mathrm{g,ex}}) - G^{\mathrm{g}}(q_{\mathrm{eq}}^{\mathrm{g,ex}}, s_{\mathrm{eq}}^{\mathrm{g,ex}}) = \sqrt{(V_{\mathrm{abs,em}}^{\mathrm{dia}})^2 + 4t^2} \qquad (7)$$

with the diabatic energy gaps[51]

$$V_{\mathrm{abs,em}}^{\mathrm{dia}} = V_0 + G_{\mathrm{s}}^{\mathrm{R}} - G_{\mathrm{s}}^{\mathrm{L}} - (\lambda_{\mathrm{q}} + \lambda_{\mathrm{s}})\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g,ex}} = V_{\mathrm{eq}}^{\mathrm{dia}} - (\lambda_{\mathrm{q}} + \lambda_{\mathrm{s}})\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g,ex}} \qquad (8)$$

3.2. Analysis of the Influence of the Solvent Polarity. Now that we have set up the explicit adiabatic framework, we turn to the study of the influence of solvent polarity on the absorption and emission transition energies.

According to eqs 7 and 8, a change in the solvent polarity affects the transition energies in two ways. First, a more polar solvent stabilizes preferentially the state with larger or more localized partial charges: in PPP, this is the zwitterionic, Z, state with respect to the neutral, N, state (cf. Scheme 1 in section 2.1.1) because of its larger dipole moment, and for charged polyenes, it is the state in which the positive charge is located on the smaller endgroup (we can already note at this point that the relative sizes of the acceptor and donor endgroups will be important). A change in the relative stabilities of the VB states alters the composition of the adiabatic ground and excited states at their respective equilibrium positions, and thus MIX depends on the solvent polarity as well. Second, a more polar solvent increases the nonequilibrium solvent reorganization energies. We assume that the electronic coupling, t, is independent of solvent polarity. Hence, when paying attention to the polarity dependence, eqs 7 and 8 become, respectively,

$$E_{\mathrm{abs,em}}(\epsilon) = \sqrt{(V_{\mathrm{abs,em}}^{\mathrm{dia}}(\epsilon))^2 + 4t^2}$$
$$V_{\mathrm{abs,em}}^{\mathrm{dia}}(\epsilon) = V_0 + \Delta G_{\mathrm{s}}(\epsilon) - (\lambda_{\mathrm{q}} + \lambda_{\mathrm{s}}(\epsilon))\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g,ex}}(\epsilon) \qquad (9)$$

where ΔG_{s} is the differential equilibrium solvation free energy of the two diabatic states, $G_{\mathrm{s}}^{\mathrm{R}} - G_{\mathrm{s}}^{\mathrm{L}}$. The detailed forms of the equilibrium solvation energies and of the nonequilibrium solvent reorganization energies will be deferred until section 5, to keep the analytic model as general as possible. The geometric reorganization energy λ_{q} does not depend on the solvent polarity and therefore plays no role in the solvatochromism interpretation. However, as has been shown elsewhere,[16] it varies with the polyene and it must be included in the model for comparison with experimental values. It can be determined in a fashion similar to that in ref 16.

3.2.1. Absorption Energy. The change of the adiabatic energy gap, E_{abs} (eq 9), with the solvent static dielectric constant, ϵ, is related to the change in the diabatic energy gap, $V_{\mathrm{abs}}^{\mathrm{dia}}$,

$$\frac{\mathrm{d}E_{\mathrm{abs}}}{\mathrm{d}\epsilon} = \frac{V_{\mathrm{abs}}^{\mathrm{dia}}}{E_{\mathrm{abs}}}\frac{\mathrm{d}V_{\mathrm{abs}}^{\mathrm{dia}}}{\mathrm{d}\epsilon} \qquad (10)$$

and the change in, $V_{\mathrm{abs}}^{\mathrm{dia}}$ (eq 9), can be decomposed into three contributions

$$\frac{\mathrm{d}V_{\mathrm{abs}}^{\mathrm{dia}}}{\mathrm{d}\epsilon} = \frac{\mathrm{d}\Delta G_{\mathrm{s}}}{\mathrm{d}\epsilon} - \mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}}\frac{\mathrm{d}\lambda_{\mathrm{s}}}{\mathrm{d}\epsilon} + \lambda_{\mathrm{s}}\frac{\mathrm{dMIX}_{\mathrm{eq}}^{\mathrm{g}}}{\mathrm{d}\epsilon} \qquad (11)$$

and the last term actually depends on $\mathrm{d}E_{\mathrm{abs}}/\mathrm{d}\epsilon$ and $\mathrm{d}V_{\mathrm{abs}}^{\mathrm{dia}}/\mathrm{d}\epsilon$ because from the definition of MIX (eq 3), $\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}}$ is related to $V_{\mathrm{abs}}^{\mathrm{dia}}$ and E_{abs}:[16]

$$\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}} = -\frac{V_{\mathrm{abs}}^{\mathrm{dia}}}{E_{\mathrm{abs}}} \qquad (12)$$

The combination of eqs 9−12 yields the polarity dependence of E_{abs},

$$\frac{dE_{abs}}{d\epsilon} = \frac{-\,\mathrm{MIX}^{g}_{eq}(\epsilon)}{1 - \dfrac{\lambda_q + \lambda_s(\epsilon)}{2|t|}(1 - \mathrm{MIX}^{g}_{eq}{}^{2}(\epsilon))^{3/2}} \left(\frac{d\Delta G_s(\epsilon)}{d\epsilon} - \mathrm{MIX}^{g}_{eq}(\epsilon)\frac{d\lambda_s(\epsilon)}{d\epsilon}\right) \quad (13)$$

The sign of this derivative gives the direction of the shift of the absorption spectrum with increasing solvent polarity: a positive derivative corresponds to a blue shift (hypsochromic shift), whereas a negative derivative corresponds to a red shift (bathochromic shift).

Because $|\mathrm{MIX}_{eq}(\epsilon)| \leq 1$, then $[1 - \mathrm{MIX}_{eq}{}^{2}(\epsilon)]^{3/2} \leq 1$. In addition, the condition $[\lambda_q + \lambda_s(\epsilon)]/(2|t|) < 1$ is always fulfilled because it is equivalent to assuming that there is a single minimum along MIX in the adiabatic ground state.[52] Thus, this denominator will always be positive.

Therefore, the sign of the derivative is determined by the numerator,

$$N_{abs}(\epsilon) \equiv -\mathrm{MIX}^{g}_{eq}(\epsilon)\left(\frac{d\Delta G_s(\epsilon)}{d\epsilon} - \mathrm{MIX}^{g}_{eq}(\epsilon)\frac{d\lambda_s(\epsilon)}{d\epsilon}\right) \quad (14)$$

The lefthand term of $N_{abs}(\epsilon)$ shows that the direction of the absorption shift is determined in part by the nature of the predominant VB state in the adiabatic ground-state composition. In the righthand term appear the two effects of the solvent polarity: on the equilibrium gap and on the solvent reorganization energy. Here we give a general discussion of this term.

In this righthand term, the change in the solvent reorganization energy is weighted by the composition of the ground state. When the solvent polarity increases, the solvent reorganization energy increases as well, which means, for example, that in the ground-state equilibrium solvent configuration the excited-state charge distribution becomes more destabilized, that is, raised in energy. When the solvent polarity increases, the further the solvent configuration is from the equilibrium configuration, the more it feels that increase in polarity. Consequently, when one VB state is largely predominant, the charge distribution in the adiabatic ground state resembles that of that VB state, and the adiabatic equilibrium solvent configuration is close to that of that same VB state. Further, the adiabatic excited state is similar to the other VB state, of which the charge distribution is thus highly out of equilibrium with the ground-state solvent configuration. Therefore, in that case, a change in the solvent polarity does not affect the ground state but destabilizes further the excited state.

In the opposite situation in which the adiabatic ground state is composed of the two VB states in similar proportions ($\mathrm{MIX}^{g}_{eq} = 0$), the two VB states also have comparable weights in the excited state. The adiabatic ground-state equilibrium solvent configuration lies between the equilibrium configurations of the L and R states. Therefore when the solvent polarity increases, both the ground- and excited-state energies will be affected in a similar way. Thus the absorption gap will not be much affected. This explains why the change in λ_s is weighted by MIX^{g}_{eq}.

3.2.2. Fluorescence Emission Energy. Before applying the relationship eq 13 to specific cases, we now derive the fluorescence equivalent of eq 13 in a fashion completely analogous to that for absorption, to determine whether the fluorescence from a molecule in its equilibrated electronic excited state exhibits a red shift or a blue shift as the solvent polarity is increased.

Within the framework of the two electronically coupled VB state model, when a given VB state is lower in energy than the other, it is predominant in the composition of the adiabatic ground state, but this also implies that it has a minority weight in the adiabatic excited state. We recall that our convention is that the MIX parameter has the same meaning for both the adiabatic ground and excited states. Therefore, for the same given configuration of the solvent polarization and of the molecular geometry, the signs of MIX^{g} and MIX^{ex} are opposite. This implies that in the counterpart of eq 12 for MIX^{ex}_{eq}, the sign differs:

$$\mathrm{MIX}^{ex}_{eq} = \frac{V^{dia}_{abs}}{E_{em}} \quad (15)$$

With this relation and eq 9, the key equation for predicting the fluorescence shifts results

$$\frac{dE_{em}}{d\epsilon} = \frac{\mathrm{MIX}^{ex}_{eq}(\epsilon)}{1 + \dfrac{\lambda_q + \lambda_s(\epsilon)}{2|t|}(1 - \mathrm{MIX}^{ex}_{eq}{}^{2}(\epsilon))^{3/2}} \left(\frac{d\Delta G_s(\epsilon)}{d\epsilon} - \mathrm{MIX}^{ex}_{eq}(\epsilon)\frac{d\lambda_s(\epsilon)}{d\epsilon}\right) \quad (16)$$

This excited-state emission relationship eq 16 differs from the analogous expression eq 13 for the ground-state case only in the sign of the second term in the denominator, for the reason explained above. The denominator is always positive, so the sign of that derivative, that is, the direction of the fluorescence shift, is determined by the numerator

$$N_{em}(\epsilon) \equiv \mathrm{MIX}^{ex}_{eq}(\epsilon)\left(\frac{d\Delta G_s(\epsilon)}{d\epsilon} - \mathrm{MIX}^{ex}_{eq}(\epsilon)\frac{d\lambda_s(\epsilon)}{d\epsilon}\right) \quad (17)$$

Equations 13 and 16 are the key relationships for predicting the direction of the absorption and fluorescence shifts when solvent polarity increases. The expressions for the equilibrium solvation energy, ΔG_s, and the solvent reorganization energy have not yet been made explicit, and therefore, there is as yet no dependence on the solvent model or on the polyene net charge (neutral or cationic). These two equations are therefore very general; they should predict the solvatochromic shifts for any molecule that can be described through a two coupled VB state model, in any kind of environment described in a continuum fashion.

4. Conditions for the Observation of an Anomalous Solvatochromism

Using eqs 13 and 16, we now seek the conditions necessary to observe an anomalous solvatochromism, that is, a shift of the absorption and emission spectra in opposite directions.

Such shifts imply that the derivatives of the absorption and emission energies with respect to solvent polarity have opposite signs, that is,

$$\frac{\mathrm{d}E_{\mathrm{abs}}}{\mathrm{d}\epsilon}\frac{\mathrm{d}E_{\mathrm{em}}}{\mathrm{d}\epsilon} < 0 \tag{18}$$

We now define the important ratio

$$\rho(\epsilon) = \frac{\dfrac{\mathrm{d}\Delta G_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon}}{\dfrac{\mathrm{d}\lambda_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon}} \tag{19}$$

and with this and the use of eqs 13 and 16, the condition eq 18 can be reformulated as

$$-\mathrm{MIX}^{\mathrm{g}}_{\mathrm{eq}}(\epsilon)\mathrm{MIX}^{\mathrm{ex}}_{\mathrm{eq}}(\epsilon)[\rho(\epsilon) - \mathrm{MIX}^{\mathrm{g}}_{\mathrm{eq}}(\epsilon)][\rho(\epsilon) - \mathrm{MIX}^{\mathrm{ex}}_{\mathrm{eq}}(\epsilon)] < 0 \tag{20}$$

If one VB state is the minor contributor in the ground state, it is the major contributor in the excited state, so $\mathrm{MIX}^{\mathrm{g}}_{\mathrm{eq}}$ and $\mathrm{MIX}^{\mathrm{ex}}_{\mathrm{eq}}$ have opposite signs, and the latter condition reduces to

$$[\rho(\epsilon) - \mathrm{MIX}^{\mathrm{g}}_{\mathrm{eq}}(\epsilon)][\rho(\epsilon) - \mathrm{MIX}^{\mathrm{ex}}_{\mathrm{eq}}(\epsilon)] < 0 \tag{21}$$

Because by definition $\mathrm{MIX}^{\mathrm{g,ex}}$ both vary between −1 and +1, to fulfill the above condition, ρ must satisfy

$$|\rho| < 1 \tag{22}$$

that is, going back to the definition eq 19, the anomalous behavior requires that, when the polarity increases, the diabatic solvent reorganization energy must increase *faster* than the equilibrium diabatic gap decreases.

If that condition is realized, there *may* exist a value of $\mathrm{MIX}^{\mathrm{g}}_{\mathrm{eq}}$ around which the solvatochromism is anomalous and eq 21 is satisfied, that is, condition eq 22 is necessary but not sufficient. In what follows, we study the implications of the condition eq 22.

For this purpose, we now introduce general expressions for the differential equilibrium solvation energy, $\Delta G_{\mathrm{s}}(\epsilon)$, and for the solvent reorganization energy, $\lambda_{\mathrm{s}}(\epsilon)$. Those expressions are valid both for the normal and charged polyenes in a solvent modeled by a linear dielectric continuum.[53] With $\mathbf{E}_{\mathrm{L}}$ and $\mathbf{E}_{\mathrm{R}}$ denoting the vacuum fields of the L and R VB states,

$$\begin{aligned}\Delta G_{\mathrm{s}}(\epsilon) &= -\frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\int_V \mathbf{E}_{\mathrm{R}}\cdot\mathbf{E}_{\mathrm{R}}\,\mathrm{d}V - \mathbf{E}_{\mathrm{L}}\cdot\mathbf{E}_{\mathrm{L}}\,\mathrm{d}V\right)\\ &= -\frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)\int_V (\mathbf{E}_{\mathrm{R}}^{\,2} - \mathbf{E}_{\mathrm{L}}^{\,2})\,\mathrm{d}V\\ \lambda_{\mathrm{s}}(\epsilon) &= \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\int_V (\mathbf{E}_{\mathrm{R}} - \mathbf{E}_{\mathrm{L}})^2\,\mathrm{d}V\end{aligned} \tag{23}$$

and the two derivatives with respect to the solvent polarity are

$$\frac{\mathrm{d}\Delta G_{\mathrm{s}}}{\mathrm{d}\epsilon} = \frac{-1}{2\epsilon^2}\int_V (\mathbf{E}_{\mathrm{R}}^{\,2} - \mathbf{E}_{\mathrm{L}}^{\,2})\,\mathrm{d}V; \qquad \frac{\mathrm{d}\lambda_{\mathrm{s}}}{\mathrm{d}\epsilon} = \frac{1}{2\epsilon^2}\int_V (\mathbf{E}_{\mathrm{R}} - \mathbf{E}_{\mathrm{L}})^2\,\mathrm{d}V \tag{24}$$

This confirms in a rigorous and general framework that a more polar solvent always increases the solvent reorganization energy, that is, it tends to increase the Stokes shift.

Figure 5. Electric dipoles used in the point dipole approach for charged polyenes.

For the ratio ρ, the prefactors vanish, leaving only the sign,

$$|\rho| = \frac{\int_V |\mathbf{E}_{\mathrm{R}}^{\,2} - \mathbf{E}_{\mathrm{L}}^{\,2}|\,\mathrm{d}V}{\int_V (\mathbf{E}_{\mathrm{R}} - \mathbf{E}_{\mathrm{L}})^2\,\mathrm{d}V} \tag{25}$$

To proceed, we need more explicit expressions for the $\mathbf{E}_{\mathrm{L}}$ and $\mathbf{E}_{\mathrm{R}}$ electric fields, taken up next.

4.1. Can the Anomalous Behavior Be Observed for Normal Polyenes? Is the anomalous behavior present for all charged polyenes? As shown in Scheme 1 (displayed in section 2.1) for the PPP, the charge distributions of the VB states can be modeled by point charges, and between the N and Z VB states, the magnitude but not the locations of these charges changes. Therefore, the electric fields of the two VB states, $\mathbf{E}_{\mathrm{N}}$ and $\mathbf{E}_{\mathrm{Z}}$, are proportional with the field of the zwitterionic Z form larger than that of the N form because of the greater extent of charge separation.

With the charge distributions shown in Scheme 1, the N and Z electric fields are

$$\mathbf{E}_{\mathrm{N}}(M) = Q_{\mathrm{N}}\left(\frac{1}{{r_{\mathrm{D}}}^2}\mathbf{u_D} - \frac{1}{{r_{\mathrm{A}}}^2}\mathbf{u_A}\right); \qquad \mathbf{E}_{\mathrm{Z}}(M) = Q_{\mathrm{Z}}\left(\frac{1}{{r_{\mathrm{D}}}^2}\mathbf{u_D} - \frac{1}{{r_{\mathrm{A}}}^2}\mathbf{u_A}\right) = \frac{Q_{\mathrm{Z}}}{Q_{\mathrm{N}}}\mathbf{E}_{\mathrm{N}}(M) \tag{26}$$

where r_{A} and r_{D} are the distances between the point M where the electric field is evaluated and each endgroup, and $\mathbf{u_A}$ and $\mathbf{u_D}$ are unit radial vectors pointing away from each endgroup and toward M. The fields $\mathbf{E}_{\mathrm{N}}$ and $\mathbf{E}_{\mathrm{Z}}$ are proportional in the ratio of the endgroup charges $Q_{\mathrm{Z}}/Q_{\mathrm{N}}$.

Then using eq 26 in eq 25 gives

$$\rho = -\frac{\left(\dfrac{Q_{\mathrm{Z}}}{Q_{\mathrm{N}}}\right)^2 - 1}{\left(\dfrac{Q_{\mathrm{Z}}}{Q_{\mathrm{N}}} - 1\right)^2} = -\frac{\dfrac{Q_{\mathrm{Z}}}{Q_{\mathrm{N}}} + 1}{\dfrac{Q_{\mathrm{Z}}}{Q_{\mathrm{N}}} - 1} \tag{27}$$

and because $|Q_{\mathrm{Z}}| > |Q_{\mathrm{N}}|$, we infer that $\rho < -1$ and the condition eq 22 for the anomalous behavior can never be fulfilled; no anomalous behavior is possible for PPP.

4.2. Is the Anomalous Behavior Present for All Charged Polyenes? Before we answer the question in the section title via the implementation of our formalism using explicit electric fields, it is useful to first examine why the simple dipole approximation fails for CPPP.

4.2.1. Failure of the Dipole Approximation for CPPP. The representation of the CPPP VB charge distributions by point charges is shown in Scheme 2 (see section 2.1). Comparing the two VB states, the negative charge remains on the counterion, while the positive charges are shifted from one endgroup to the other. Hence, the location of the charges changes, but their magnitudes remain unchanged, thus differing in both respects from the normal polyene case in section 4.1.

Of course, as in the normal polyene case, a point dipole could here as well be associated with each VB state, to give a simplified model of the charge distribution, as represented in Figure 5.

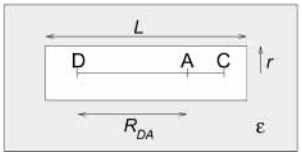


Figure 6. Cylindrical cavity of length L and radius r around the charged polyene and its counterion embedded in a dielectric continuum of dielectric constant ϵ.

However, the comparison of the interaction energies of these two dipoles, μ_A and μ_D, with the solvent would lead to the wrong physical image. Indeed, beause of the larger charge separation in the D state, $\mu_D \gg \mu_A$ and the solvation energy of the D state would be much larger than that of the A state. In fact, provided that the two endgroups have similar sizes, the solvation free energies of both VB states are very close: the distance between the point charges is large enough so that the charges can be considered to be solvated nearly independently (this is obvious for the two endgroups that are separated by a long polyenic chain; this is more of an approximation for the endgroup next to the counterion but our goal here is only to extract the origin of the failure of the point dipole picture for charged polyenes). The point dipole representation is an effective model that is qualitatively valid for the normal polyenes for which the magnitude of the partial charges changes between the two VB states but that is invalid for the charged case, for which the difference in the dipole moments of the two states is only due to the shift of a charge, which has little effect on the solvation energy.

4.2.2. Influence of the Relative Donor and Acceptor Sizes and Separation. To determine whether the anomalous solvatochromism is a general behavior of the CPPP, we need to express the electric field associated with each of the two VB states displayed in Scheme 2 (see section 2.1),

$$\mathbf{E}_L = \frac{Q_L}{{r_A}^2}\mathbf{u_A} + \frac{1-Q_L}{{r_D}^2}\mathbf{u_D} - \frac{1}{{r_C}^2}\mathbf{u_C}; \qquad \mathbf{E}_R = \frac{1-Q_R}{{r_A}^2}\mathbf{u_A} + \frac{Q_R}{{r_D}^2}\mathbf{u_D} - \frac{1}{{r_C}^2}\mathbf{u_C} \quad (28)$$

In contrast to the situation for the PPP, the two electric fields are not proportional.

The value of $|\rho|$ (eq 25) depends on the integration domain, that is, on the allowed volume for the solvent around the polyene. To analyze this dependence, we assume that the polyene is embedded in a cylindrical cavity with finite radius r and length L (see Figure 6). In addition, we consider the limiting case where $Q_R = Q_L = 1$.

Effect of a Change in the Cavity Diameter. For a fixed donor−acceptor distance, R_{DA}, we first examine the influence of an increase in the cavity radius r. The influence on $|\rho|$ (eq 25), and therefore on the presence of an anomalous behavior, is presented in Figure 7. For small r, the solvent molecules are allowed to come close to the molecular axis between the two sites of the charge transfer, the A and D groups; the charge distribution that is seen by the solvent can be well approximated by separate point charges, $|\rho| < 1$, and the anomalous behavior is possible. However, when r increases, the solvent molecules are kept further away from the charges and the effective electric field that they feel resembles more and more that of a dipole formed by the positive charge of the polyene and the negative charge of the counterion. Hence, $|\rho|$ becomes larger than one, and no anomalous behavior is possible, as was shown in section 4.

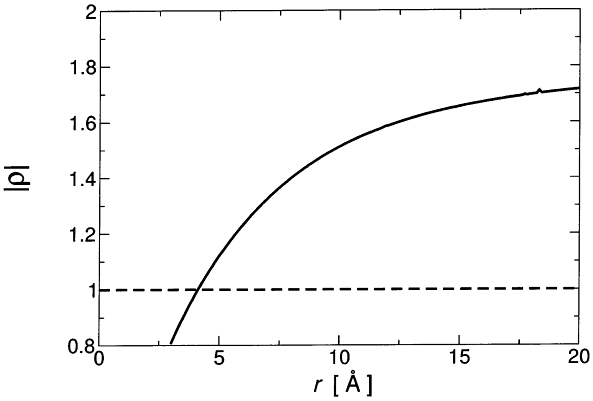


Figure 7. Effect of a change in the cavity radius r on $|\rho|$ for $R_{DA} = 10$ Å, $R_{AC} = 4$ Å, $L = R_{DA} + R_{AC} + 2r$, and $Q_R = Q_L = 1$.

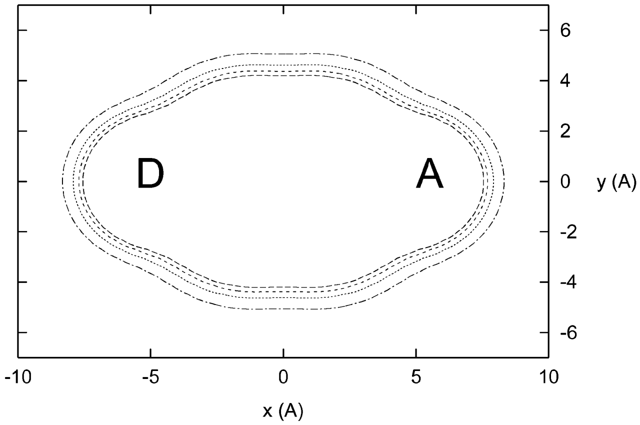


Figure 8. Contour plot of $(\mathbf{E}_{\text{pointcharge}} - \mathbf{E}_{\text{dipole}})^2$ with the electric fields corresponding to the difference between the charge distributions of the L and R VB states for a CPPP in the point charge and in the point dipole representation with a spacing of 2×10^{-4} au.

We now consider the electric field $\mathbf{E}_R - \mathbf{E}_L$ corresponding to the difference between the charge distributions in the L and R VB states, which appears in the definition of $|\rho|$ (eq 25). Independently of the cavity shape, the difference at each point between the point dipole and point charges representation of this field can help to determine which volume around the polyene must be forbidden to the solvent to suppress the anomalous behavior. Figure 8 displays the square of the difference between the point dipole and point charges electric fields $(\mathbf{E}_{\text{pointcharge}} - \mathbf{E}_{\text{dipole}})^2$ in a plane. This confirms that the area responsible for the difference is close to the molecular axis.

We therefore predict that the anomalous behavior vanishes for charged “polyenes” with bulky conjugated bridges. Naturally, such bridges can no longer be polyenic indeed, but our whole approach is valid for any kind of conjugated bridge. This disappearance of the anomalous behavior is exactly what is observed for several cationic conjugated donor−acceptor molecules with bulky bridges, like rhodamine 700, thionine, or resorufin.[47] Those molecules are well-known donor−acceptor compounds and belong to the (wide) family of charged push−pull molecules. Our approach can thus successfully describe their behavior, whereas Fromherz’s approach relied on the assumption that the sum $E_{abs} + E_{em}$ remains constant,[42] which is not the case here.

Effect of a Change in the Cavity Length. For a fixed cavity radius ($r = 5$ Å), we now examine the influence of an increase of the donor−acceptor distance, R_{DA}, and thus an elongation of the cavity. Figure 9 shows that $|\rho|$ regularly decreases with

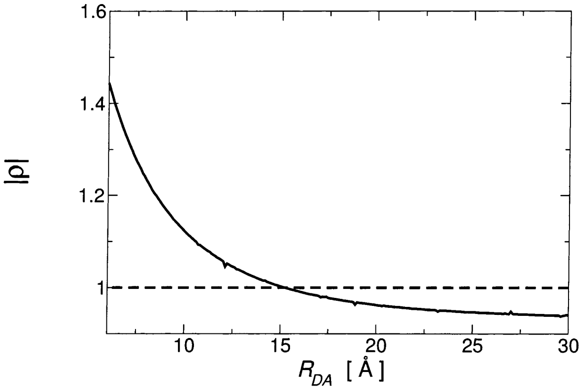


Figure 9. Effect of a change in the donor−acceptor distance, R_{DA}, on $|\rho|$ for $r = 5$ Å, $R_{\mathrm{AC}} = 4$ Å, $L = R_{\mathrm{DA}} + R_{\mathrm{AC}} + 2r$, and $Q_{\mathrm{R}} = Q_{\mathrm{L}} = 1$.

increasing length R_{DA}; the two sites D and A between which the charge transfer occurs move farther apart, and the charge distribution resembles less and less the one of a point dipole, and more and more that of two widely separated point charges. This explains the transition between a regime in which no anomalous behavior is possible ($|\rho| > 1$) to a regime in which it is allowed ($|\rho| < 1$). We therefore predict that for extremely short conjugated bridges, the anomalous effect should disappear. However, for all of the CPPP molecules of which we are aware, the distance between the endgroup centers is too large to allow such an effect to be observed. Experimental investigation of CPPP molecules with shorter separations would thus be of interest.

5. Detailed Model Applications

We now apply the previous results more quantitatively and derive more detailed expressions for the solvation and solvent reorganization free energies that enter in the definition of ρ, eq 19. Again, the polyene, normal or charged, is still described by two electronically coupled VB states. The solvent is approximated by a dielectric continuum, and the Marcus−Born model[54] is used to describe the charge transfer in solution. The change in the bonding pattern between the two VB states is still described by a geometric coordinate q.

5.1. Neutral Polyenes. In the Marcus−Born model of solvation, the solvation free energy of the two VB states presented in Scheme 1 for the PPP case (displayed in section 2.1) is

$$G_{\mathrm{s}}^{\mathrm{N,Z}}(\epsilon) = -\left(1 - \frac{1}{\epsilon}\right)Q_{\mathrm{N,Z}}^{2}\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right) \quad (29)$$

where $Q_{\mathrm{N,Z}}$ is the charge magnitude on the donor and acceptor groups in the neutral and zwitterionic states, r_{D} and r_{A} are the radii of the solvent cavities surrounding those two endgroups, and R_{DA} is the distance between their centers. Thus, the differential solvation energy of the two VB states is

$$\Delta G_{\mathrm{s}}(\epsilon) = G_{\mathrm{s}}^{\mathrm{Z}}(\epsilon) - G_{\mathrm{s}}^{\mathrm{N}}(\epsilon) = -\left(1 - \frac{1}{\epsilon}\right)(Q_{\mathrm{Z}}^{2} - Q_{\mathrm{N}}^{2})\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right) \quad (30)$$

In the same model, the (diabatic) solvent reorganization energy is

$$\lambda_{\mathrm{s}}(\epsilon) = \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon}\right)(Q_{\mathrm{Z}} - Q_{\mathrm{N}})^{2}\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right) \quad (31)$$

The two corresponding derivatives with respect to the solvent dielectric constant are then

$$\frac{\mathrm{d}\Delta G_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon} = -\frac{1}{\epsilon^{2}}(Q_{\mathrm{Z}}^{2} - Q_{\mathrm{N}}^{2})\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right)$$

$$\frac{\mathrm{d}\lambda_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon} = \frac{1}{\epsilon^{2}}(Q_{\mathrm{Z}} - Q_{\mathrm{N}})^{2}\left(\frac{1}{2r_{\mathrm{D}}} + \frac{1}{2r_{\mathrm{A}}} - \frac{1}{R_{\mathrm{DA}}}\right) \quad (32)$$

Because the zwitterionic VB state has a much larger dipole moment compared to the neutral VB state, a more polar solvent preferentially stabilizes the Z state and reduces the equilibrium diabatic gap ΔG_{s}. This can be seen from eq 32, in which the larger magnitude of the end charges in the Z state implies that the derivative is negative.

The replacement of eq 32 in the definition of ρ, eq 19, confirms the result, eq 27, that was found in the general case of a normal polyene with the point charge description: when the solvent becomes more polar, the equilibrium diabatic gap ΔG_{s} decreases more rapidly than the diabatic solvent reorganization energy increases. The *direction* of the shifts is governed by the changes in the equilibrium energy gap, which tend to shift both spectra in the same direction; but the *amplitude* of those shifts is affected by the nonequilibrium contribution arising from the larger solvent reorganization energy, which tends to increase the Stokes shift.

5.2. Charged Polyenes. We now turn to the case of a charged polyene and again consider the key ratio ρ, eq 19. As explained in section 3, we can safely ignore the counterion, essentially because it is solvated independently.

Because the charge distribution of the CPPP molecule now corresponds to a net charge and not a dipole, the solvation free energies differ from those for normal polyenes. Within the Marcus−Born model, the solvation free energies of the L and R VB states can be expressed as

$$G_{\mathrm{s}}^{\mathrm{L}}(\epsilon) = -\left(1 - \frac{1}{\epsilon}\right)\left(\frac{Q_{\mathrm{L}}^{2}}{2r_{\mathrm{A}}} + \frac{(1 - Q_{\mathrm{L}})^{2}}{2r_{\mathrm{D}}} + \frac{Q_{\mathrm{L}}(1 - Q_{\mathrm{L}})}{R_{\mathrm{DA}}}\right)$$

$$G_{\mathrm{s}}^{\mathrm{R}}(\epsilon) = -\left(1 - \frac{1}{\epsilon}\right)\left(\frac{(1 - Q_{\mathrm{R}})^{2}}{2r_{\mathrm{A}}} + \frac{Q_{\mathrm{R}}^{2}}{2r_{\mathrm{D}}} + \frac{Q_{\mathrm{R}}(1 - Q_{\mathrm{R}})}{R_{\mathrm{DA}}}\right) \quad (33)$$

where $Q_{\mathrm{L,R}}$ is the charge magnitude as defined in Scheme 2.

Thus, the difference between the solvation energies of the two VB states is

$$\Delta G_{\mathrm{s}}(\epsilon) = G_{\mathrm{s}}^{\mathrm{R}}(\epsilon) - G_{\mathrm{s}}^{\mathrm{L}}(\epsilon) = -\frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)(Q_{\mathrm{L}} + Q_{\mathrm{R}} - 1)\left[(Q_{\mathrm{R}} - Q_{\mathrm{L}})\left(\frac{1}{r_{\mathrm{A}}} + \frac{1}{r_{\mathrm{D}}} - \frac{2}{R_{\mathrm{DA}}}\right) + \left(\frac{1}{r_{\mathrm{D}}} - \frac{1}{r_{\mathrm{A}}}\right)\right] \quad (34)$$

Here as in the case of a globally neutral polyene, the (diabatic) solvent reorganization energy corresponds to a charge transfer from one endgroup to the other, so the solvent reorganization energy remains formally the same as that in eq 31, and the only difference is in the expression of the charge-transfer magnitude in terms of the new endgroup charges

$$\lambda_{\mathrm{s}}(\epsilon) = \frac{1}{2}\left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon}\right)(1 - Q_{\mathrm{L}} - Q_{\mathrm{R}})^{2}\left(\frac{1}{r_{\mathrm{D}}} + \frac{1}{r_{\mathrm{A}}} - \frac{2}{R_{\mathrm{DA}}}\right) \quad (35)$$

The two corresponding derivatives with respect to the solvent dielectric constant are

$$\frac{\mathrm{d}\Delta G_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon} = -\frac{1}{2\epsilon^{2}}(Q_{\mathrm{L}} + Q_{\mathrm{R}} - 1)\left[(Q_{\mathrm{R}} - Q_{\mathrm{L}})\left(\frac{1}{r_{\mathrm{A}}} + \frac{1}{r_{\mathrm{D}}} - \frac{2}{R_{\mathrm{DA}}}\right) + \left(\frac{1}{r_{\mathrm{D}}} - \frac{1}{r_{\mathrm{A}}}\right)\right]$$

$$\frac{\mathrm{d}\lambda_{\mathrm{s}}(\epsilon)}{\mathrm{d}\epsilon} = \frac{1}{2\epsilon^{2}}(Q_{\mathrm{L}} + Q_{\mathrm{R}} - 1)^{2}\left(\frac{1}{r_{\mathrm{D}}} + \frac{1}{r_{\mathrm{A}}} - \frac{2}{R_{\mathrm{DA}}}\right) \qquad (36)$$

We pause to note that for $Q_{\mathrm{L}} = Q_{\mathrm{R}} = 0.5$, the two derivatives are zero because the two VB states are the two limiting forms of a cyanine structure.[55]

Here again, as in the case of normal polyenes, eq 36 shows that the CPPP case solvent reorganization energy increases when the polarity increases, which has already been shown in the general case in eq 24. But the key difference with normal polyenes is that a more polar solvent does *not* systematically reduce the diabatic equilibrium energy gap; the change in the energy gap depends on the relative sizes and charges of the endgroups, as can be seen from eq 36. A widening diabatic equilibrium energy gap tends to shift both the absorption and fluorescence spectra to the blue, while a narrowing energy gap tends to shift both spectra to the red. (Here, one should keep in mind that because the equilibrium energy gap is defined as $\Delta G_{\mathrm{s}} = G^{\mathrm{R}} - G^{\mathrm{L}}$, a positive derivative of the gap with respect to the dielectric constant means that the gap widens only when this gap is positive, that is when L is more stable than R and $\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}} < 0$.) Therefore, in a more polar solvent, if the diabatic equilibrium energy gap widens, both this effect and the larger solvent reorganization energy tend to shift the absorption spectrum to the blue. But for the fluorescence energy, the widening of the diabatic equilibrium energy gap tends to shift it to the blue, while the larger solvent reorganization energy tends to shift it to the red.

The solvatochromism direction is governed by the ratio ρ, eq 19, of $\mathrm{d}\Delta G_{\mathrm{s}}/\mathrm{d}\epsilon$ and $\mathrm{d}\lambda_{\mathrm{s}}/\mathrm{d}\epsilon$, eq 36, and its value is clearly determined by the relative sizes and charges of the endgroups.

To add some insight on our conclusions both for the normal and charged polyenes, the evolution with solvent polarity of some key quantities are plotted in Figure 10. Parameters of the prototypical polyenes used for these plots are provided in Table 1. The two upper panels, Figure 10a, first show that, as expected, in the neutral PPP case, both the absorption and emission transition energies decrease when the solvent polarity increases (red shift), while in the charged CPPP case, the absorption energy increases and the emission energy decreases. Figure 10b details the different contributions to the diabatic gap, V^{dia}; this highlights that in the PPP the solvatochromic behavior is due to the decrease of the equilibrium diabatic gap, $V_{\mathrm{eq}}^{\mathrm{dia}}$, in more polar solvents, compared to which the change in solvent reorganization energy, λ_{s}, remains negligible. On the other hand, in CPPP, the diabatic equilibrium gap, $V_{\mathrm{eq}}^{\mathrm{dia}}$, remains constant, while the increase in the solvent reorganization energy governs the solvatochromic behavior. We recall that though we discuss here the more intuitive diabatic quantities our theory is fully adiabatic and all adiabatic quantities can be inferred with eq 8. In addition, Figure 10c shows the change in the $\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g,ex}}$ values: while in the PPP case, a more polar solvent reduces the free energy gap between the two VB states and increases the mixing in the composition of the adiabatic electronic wave functions, in the CPPP case, the nearly constant equilibrium adiabatic gap and the increasing solvent reorganization energies tend to increase the weight of the more stable VB state in the adiabatic ground state and of the less stable VB state in the adiabatic excited state. A last key feature to note is the much smaller sensitivity of the electronic structure upon solvent polarity for the CPPP compounds than for the normal polyenes.[48,49]

5.3. Role of the Endgroup Sizes. Here we examine the influence of the endgroup sizes on the existence of an anomalous solvatochromism, restricting our attention to the CPPP case. For ease of exposition, we use simple charge distributions for the two VB states with a full negative charge either on the acceptor or on the donor group, that is, $Q_{\mathrm{R}} = Q_{\mathrm{L}}$. From eq 36, it is clear that for the same endgroup size case $\rho = 0$, and the condition $|\rho| < 1$ (see eq 22) for the possibility of an anomalous behavior is fulfilled. In addition, for $\rho = 0$, from eq 21, the condition for the existence of the anomalous behavior reduces to

$$\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}}(\epsilon)\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{ex}}(\epsilon) < 0 \qquad (37)$$

which is always the case because by definition $\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{g}}(\epsilon)$ and $\mathrm{MIX}_{\mathrm{eq}}^{\mathrm{ex}}(\epsilon)$ have opposite signs. Thus for any value of the solvent polarity, the absorption and emission spectra shift in opposite directions.

But if one endgroup is larger than the other, then the VB state in which the charge is located on the smaller endgroup is preferentially solvated by a polar solvent. This modifies the equilibrium energy gap between the diabatic states. From eq 8, there are now two competing effects, the increase in the solvent reorganization energy λ_{s} and the change in the diabatic equilibrium energy gap $V_{\mathrm{eq}}^{\mathrm{dia}}$. If the difference between the solvation energies of the two VB states is large enough to compensate for the increase in the solvent reorganization energy, the change in the adiabatic equilibrium energy gap governs the spectral shifts (as in the case of PPP); otherwise, the directions of the shifts only reflect the increase in the solvent reorganization energy.

For example, for a CPPP with $Q_{\mathrm{R}} = Q_{\mathrm{L}}$ and $r_{\mathrm{D}} < r_{\mathrm{A}}$ and with a distance between the endgroups R_{DA} much larger than their radii $r_{\mathrm{A,D}}$, from use of eq 32, the condition $|\rho| < 1$ implies

$$\frac{1}{r_{\mathrm{D}}} - \frac{1}{r_{\mathrm{A}}} < \frac{1}{2}\left(\frac{1}{r_{\mathrm{D}}} + \frac{1}{r_{\mathrm{A}}}\right) \qquad (38)$$

that is,

$$r_{\mathrm{D}} > \frac{r_{\mathrm{A}}}{3} \qquad (39)$$

Thus if the donor cavity is more than three times smaller than the acceptor cavity, the anomalous behavior disappears.

Experimentally, for all of the charged push−pull polyenes of which we are aware,[26,30,33,47] the donor and acceptor endgroups are similar in size, and this effect has not yet been observed. While our results indicate that a rather large size disparity for donor and acceptor groups is required, it could nonetheless be of interest to search for this effect experimentally.

6. Charged Polyenes and NLO

We now apply the preceding theory to examine the NLO properties of CPPP and their contrast with those of PPPP. As we see, it is now a simple matter to discuss these, given our theoretical formulation. The NLO properties (α, β, γ, ...) all depend on the absorption energy and not on the emission energy. Because the main interest of the anomalous behavior are the shifts of the absorption and emission energies in opposite

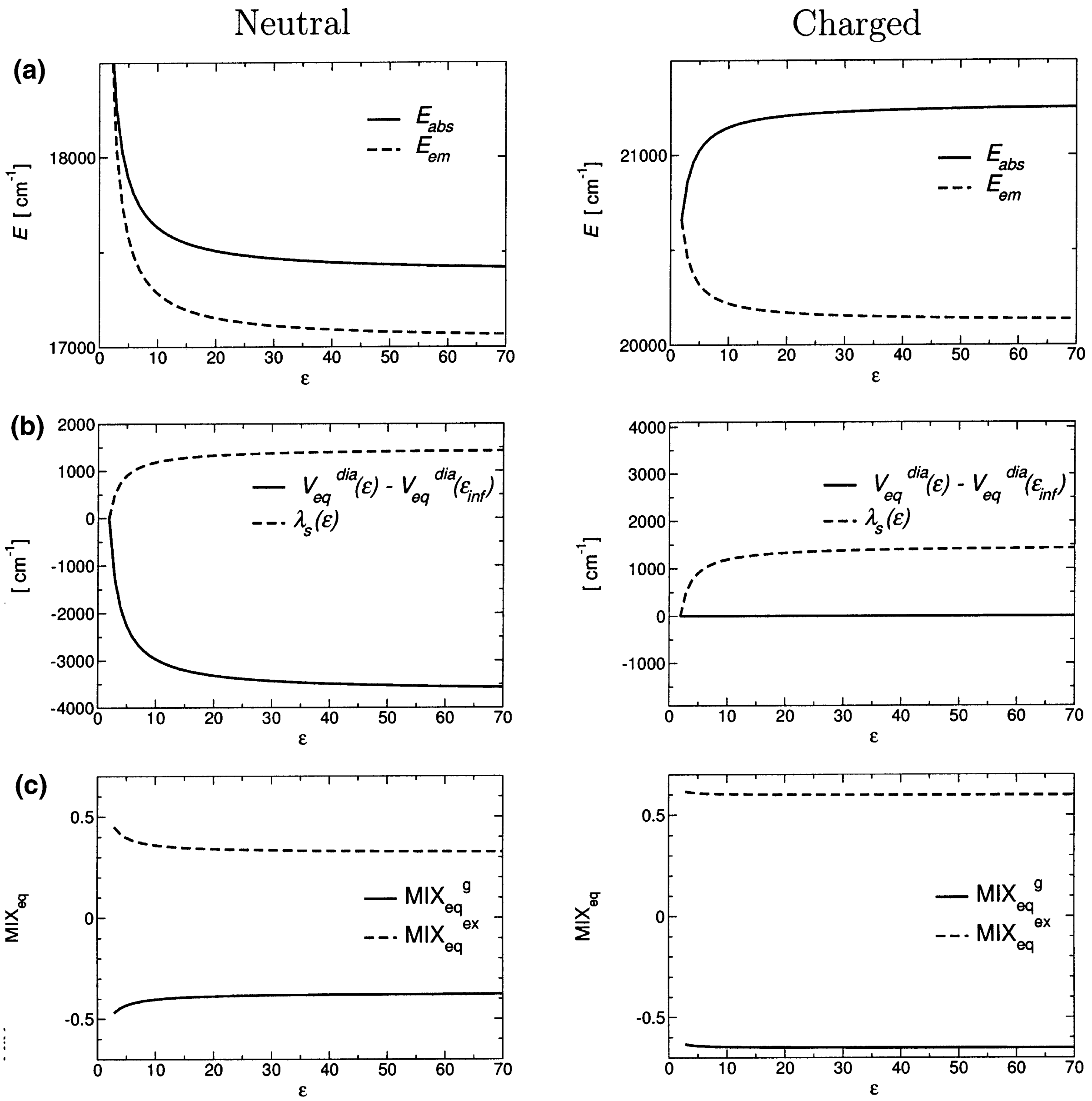


Figure 10. Spectroscopic behavior with solvent polarity of a neutral and a charged push−pull polyene, of which the key parameters are detailed in Table 1: (a) E_{abs}, E_{em}; (b) V_{eq}^{dia}, λ_s; (c) MIX_{eq}^{g}, MIX_{eq}^{ex}. For each property, the scale, even if shifted, is identical for the neutral and charged cases.

TABLE 1: Parameters of the Prototypical Polyenes the Behaviors of Which Are Presented in Figures 10 and 11

parameter	neutral	charged
r_A (Å)	4	4
r_D (Å)	4	4
R_{DA} (Å)	10	10
V_0 (eV)	1.6	1.6
t (eV)	1	1
Q_A^L	−0.3	+0.7
Q_D^L	+0.3	+0.3
Q_A^R	−0.7	+0.3
Q_D^R	+0.7	+0.7
λ_q (eV)	0	0

directions, the behavior of the NLO properties with changing solvent polarity is automatically less dramatic than the behavior of the absorption and emission spectra. Nonetheless, there are important polarity effects and consequences for the optimal molecular design for the NLO properties, now discussed.

For normal polyenes, the first-order polarizability is given by (see ref 16)

$$\alpha = \frac{2t^2\mu_{CS}^{\ 2}}{(E_{abs}(\epsilon))^3} \tag{40}$$

where μ_{CS} is the charge shift dipole moment, $\mu_{CS} = \mu_Z - \mu_N$. For charged push−pull polyenes, the charge distribution in one VB state is not dipolar but corresponds to a positive unit charge (see Scheme 2 presented in section 2.1). The polarizability definition, eq 40, still holds for charged polyenes, as we now briefly demonstrate.

From the definition of the ground-state wave function in eq 3, the charges on each endgroup are

$$Q_D = \frac{1 - MIX_g}{2}(1 - Q_L) + \frac{1 + MIX_g}{2}Q_R$$

$$Q_A = \frac{1 - MIX_g}{2}Q_L + \frac{1 + MIX_g}{2}(1 - Q_R) \tag{41}$$

We now choose the particular case in which $Q_R = Q_L = 1$ because this simplifies greatly the notation; the generalization to other charge magnitudes is straightforward. Equation 41 reduces to

$$Q_{D,A} = \frac{1}{2}(1 \pm \mathrm{MIX}_g) \tag{42}$$

If the polyene is placed in a constant external electric field **F** derived from the electric potential Ψ with $\Psi_{D,A}$ being the electric potential felt by each endgroup, the component of the ground-state potential energy due to that electric field is

$$V_g = Q_D\Psi_D + Q_A\Psi_A = \frac{1}{2}(\Psi_D + \Psi_A) + \frac{1}{2}\mathrm{MIX}_g(\Psi_D - \Psi_A) \tag{43}$$

Because the electric field **F** is constant throughout space,

$$\Psi_D - \Psi_A = (\mathbf{r}_D - \mathbf{r}_A)\nabla\Psi = -(\mathbf{r}_D - \mathbf{r}_A)\mathbf{F} = -\mu_{CS}\mathbf{F} \tag{44}$$

where $\mathbf{r}_D$ and $\mathbf{r}_A$ are the positions of the two endgroups and where the charge shift dipole moment is defined as

$$\mu_{CS} = \mathbf{r}_D - \mathbf{r}_A \tag{45}$$

with the elementary charge e implicit. This is the dipole moment of the charge distribution resulting from the difference between the charge distributions of the R and L forms.

By definition, the polarizability α is $\alpha = -{}^1/_2\, \partial^2 V_g/\partial F^2$ taken for $F = 0$. We only consider the case in which the electric field **F** is parallel to the D−A molecular axis, that is, $\alpha = \alpha_{zz}$ with μ_{CS} positive when $\mathbf{r}_D - \mathbf{r}_A$ has the same orientation as **F**, like in the normal polyene case. Because the ground state MIX function is

$$\mathrm{MIX}_g = -\frac{V_R - V_L}{\sqrt{(V_R - V_L)^2 + 4t^2}} \tag{46}$$

this yields

$$\frac{\mathrm{dMIX}_g}{\mathrm{d}F} = -\frac{4t^2\mu}{((V_R - V_L)^2 + 4t^2)^{3/2}} \tag{47}$$

and thus

$$\alpha = \frac{2t^2{\mu_{CS}}^2}{(E_{abs}(\epsilon))^3} \tag{48}$$

Because both the coupling, t, and the VB state dipole moments are polarity independent, the polarity dependence of α is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\epsilon} = \frac{-6t^2{\mu_{CS}}^2}{(E_{abs}(\epsilon))^4}\frac{\mathrm{d}E_{abs}}{\mathrm{d}\epsilon} \tag{49}$$

The first ratio in the right-hand term is negative, so when E_{abs} increases, that is, when the absorption spectrum is blue-shifted, α decreases. That relation is valid for all kinds of polyenes, neutral or charged. Unlike normal polyenes, for most of which, with increasing solvent polarity, the absorption spectrum is red-shifted and therefore α increases, charged polyenes exhibiting the anomalous behavior will display the opposite trend for α: α *decreases* with a larger solvent polarity.

In a similar fashion, the second-order polarizability can be derived (see ref 16)

$$\beta = \frac{6V_{eq}^{dia}t^2{\mu_{CS}}^3}{(E_{abs}(\epsilon))^5} \tag{50}$$

Note that β depends on the sign of μ_{CS} and therefore on the orientation of the molecule with respect to the electric field.

From use of eq 12, the derivative of β with respect to solvent polarity is

$$\frac{\mathrm{d}\beta}{\mathrm{d}\epsilon} = \mathrm{MIX}_{eq}^{g}\frac{30t^2{\mu_{CS}}^3}{{E_{abs}}^5}\left({\mathrm{MIX}_{eq}^{g}}^2 - \frac{1}{5}\right)\frac{\mathrm{d}E_{abs}}{\mathrm{d}\epsilon} \tag{51}$$

As shown in Figures 10c and 11b for the model neutral polyene, $\mathrm{MIX}_{eq}^{g} = -1/\sqrt{5}$ corresponds to a maximum of β. Because β is proportional to $\mathrm{d}E/\mathrm{d}\epsilon$, the β values of PPP and CPPP follow *opposite* trends with solvent polarity for similar values of MIX_{eq}^{g}. Whereas for PPP β reaches a maximum at $\mathrm{MIX}_{eq}^{g} = -1/\sqrt{5}$, it becomes a minimum for CPPP. It is important to note however that the trends are opposite *only* if the MIX_{eq}^{g} parameter describing the ground-state electronic structure is the *same* in the PPP and the CPPP. But this will generally not be the case because MIX_{eq}^{g} is much more sensitive to solvent polarity in the PPP than in the CPPP (see Figure 10c). Thus, for the PPP example studied in Figures 10 and 11, $|\mathrm{MIX}_{eq}^{g}|$ decreases and crosses the critical value $1/\sqrt{5}$, and hence, β reaches a maximum; on the other hand, in the CPPP case, $|\mathrm{MIX}_{eq}^{g}|$ is nearly constant and remains larger than $1/\sqrt{5}$ for any solvent polarity, and hence, the extremum is never reached. Therefore, these two polyenes do not exhibit opposite trends for the β polarity dependence (except in the very low solvent polarity range, see Figure 11). As a final remark, we note that there is an advantage of CPPP over PPP for the molecular engineering of optimized β values because in this case it is possible to act not only on the sign of the $({\mathrm{MIX}_{eq}^{g}}^2 - {}^1/_5)$ term but also on the sign of $\mathrm{d}E_{abs}/\mathrm{d}\epsilon$, which can be different for the former but is fixed for the latter (see section 4.2).

The third-order polarizability is given by (see ref 16)

$$\gamma = \frac{24({V_{eq}^{dia}}^2 - t^2)t^2{\mu_{CS}}^4}{{E_{abs}}^7} \tag{52}$$

and with use of eq 12 again, its derivative with respect to solvent polarity is

$$\frac{\mathrm{d}\gamma}{\mathrm{d}\epsilon} = -\frac{210t^2{\mu_{CS}}^4}{{E_{abs}}^6}\left({\mathrm{MIX}_{eq}^{g}}^2 - \frac{3}{7}\right)\frac{\mathrm{d}E_{abs}}{\mathrm{d}\epsilon} \tag{53}$$

This shows that for both normal and charged polyenes, the composition $\mathrm{MIX}_{eq}^{g} = \pm\sqrt{{}^3/_7}$ corresponds to an extremum in γ.

The comparison of the γ trend between PPP and CPPP relies on the same arguments as the β trend, except that the value of MIX_{eq}^{g} at the extremum of γ is different than the value of MIX_{eq}^{g} at the extremum of β.

These simple model calculations serve to emphasize the important point that the conditions that would be optimal to maximize a particular nonlinear response for a CPPP can be quite different from those of a PPP. They also show that the NLO properties for CPPP are much less sensitive to the solvent

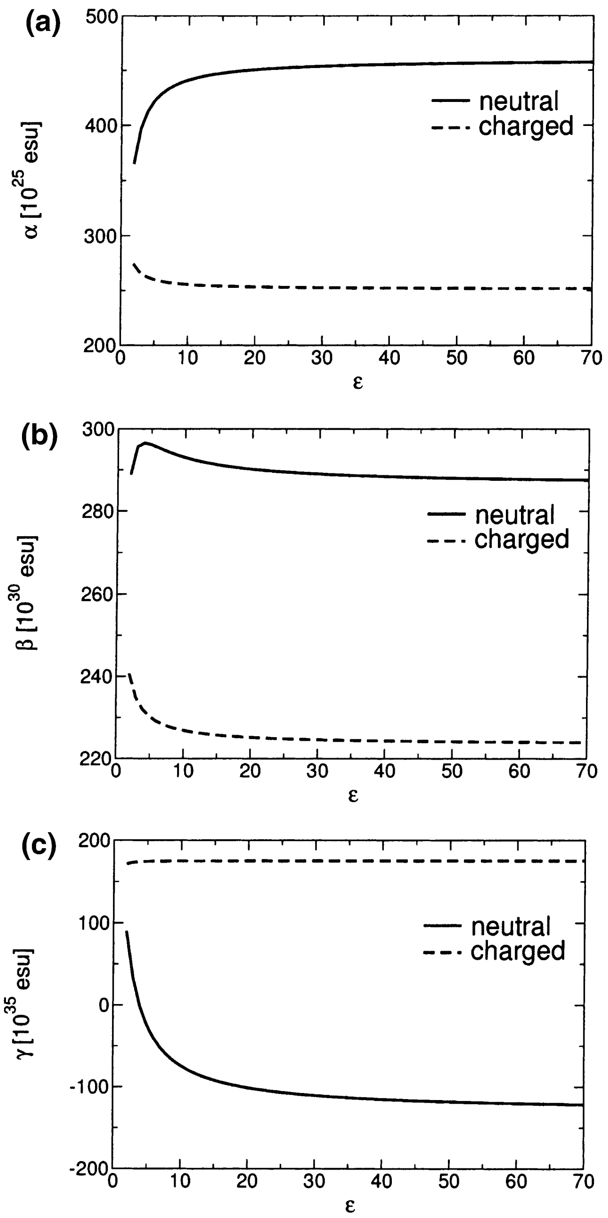


Figure 11. NLO properties, α, β, and γ, when the solvent polarity is varied for a neutral and a charged push−pull polyene, of which the key parameters are detailed in Table 1.

polarity than those in the neutral case because of the vanishing differential equilibrium solvation, for example, for similarly sized donor and acceptor groups. The remarkable stability of the CPPP NLO properties with respect to a change in their environment would initially suggest that they are in fact not such good probes of membrane potential. Indeed, this weak sensitivity toward the environment is observed experimentally for the solvatochromism of CPPP[26] as well; the spectral shifts with increasing solvent polarity are much smaller than what is commonly observed for PPP (See Figure 10a). Despite this reduced sensitivity, CPPP are preferred to PPP for biological applications because their structure with a polar head and a hydrophobic chain makes them easy to insert in a biological membrane. Thus, it is important to understand how the sensitivity can be increased, and our theoretical treatment suggests several promising directions for this: use donor and acceptor groups with very different sizes or use bulky conjugated bridges (see section 4.2.2). A further possibility (see section 4.2.2) is to employ short D−A distances, but this is less likely to be effective because this would probably produce molecules that are less easy to insert in a membrane.

7. Concluding Remarks

We have developed a reasonably general theoretical formulation for the anomalous absorption and fluorescence solvatochromic properties of charged push−pull polyenes in solution: with increasing solvent polarity, a blue shift in absorption and a red shift in emission. The theory includes the strong electronic coupling between two VB states to describe the electronic structure and involves the treatment of the nonequilibrium solvent polarization necessary to discuss such Franck−Condon transitions, as well as an internal geometric coordinate describing shifts of the alternating carbon single−double bonding pattern in the intervening π chain between the electron donor and acceptor.

The formulation successfully predicts both when anomalous solvatochromic behavior should be observed and when it should not. We have suggested several aspects important in this connection, that is, the relative donor and acceptor sizes and separation (see section 4.2.2), which should be explored experimentally. Further, it can be directly applied to predict the solution polarity dependence of the nonlinear optical properties of the charged push−pull polyenes, of which the large values are due to the strong electronic coupling between the VB states. These results should be useful in molecular engineering issues for such charged polyenes. Further, they can be compared to experiment—along the lines of the comparison made for neutral push−pull polyenes in ref 17—when data become available.

We noted at the conclusion of section 6 that, at least in the relatively common case in which the equilibrium solvation of the ground and excited states for a CPPP is similar, the NLO properties are much less sensitive to the environmental polarity for the CPPP compared to the neutral case. Because this would severely reduce the value of CPPP molecules as probes for, , for example, membrane potentials, attention must be paid to molecular engineering issues designed to increase the sensitivity. Several suggestions have been made on the basis of our developed theory.

Perhaps the most interesting and important area where further advances are required is that of construction of a proper theoretical framework for spectroscopic probes of biological systems such as membranes. Such environments are strongly inhomogeneous, and while our theoretical formulation was largely developed for the CPPP in homogeneous environments such as polar solvents, a significant portion of the theoretical framework was not restricted to a homogeneous environment. The combination of the basic formulation presented here with a Poisson−Boltzmann[56] description of the inhomogeneous environment should provide a useful formulation for the treatment of CPPP spectroscopy in biological media and is under development.

Acknowledgment. This work was supported in part by the CNRS and by NSF Grant CHE-0108314. M.B.D. acknowledges CNRS for financial support (*soutien jeune équipe*).

References and Notes

(1) Michl, J.; Klessinger, M. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, 1995.

(2) For current trends in molecular NLO, see, for instance, the special issue of *Chemical Physics* devoted to molecular nonlinear optics: *Chem. Phys.* **1999**, *245*.

(3) Shi, Y. Q.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119−122. Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843−845.

(4) He, G. S.; Xu, G. C.; Prasad, P. N.; Reinhardt, B. A.; Bhatt, J. C.; Dillard, A. G. *Opt. Lett.* **1995**, *20*, 435−437.

(5) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73−76.

(6) For a recent review, see, for instance: Wolff, J. J.; Wortmann, R. *Adv. Org. Chem.* **1999**, *32*, 121−217.

(7) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortmann, R. *Chem.*−*Eur. J.* **1997**, *3*, 1091−1104. Alain, V.; Rédoglia, S.; Blanchard-Desce, M.; Lebus, S.; Lukaszuk, K.; Wortmann, R.; Gubler, U.; Bosshard, C.; Gunter, P. *Chem. Phys.* **1999**, *245*, 51−71.

(8) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *1912*, 245−250.

(9) Bourhill, G.; Brédas, J.; Cheng, L.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, *116*, 2619−2620.

(10) Mikkelsen, K. V.; Luo, Y.; Ågren, H.; Jørgensen, P. *J. Chem. Phys.* **1994**, *100*, 8240−8250. Mikkelsen, K. V.; Sylvester-Hvid, K. O. *J. Phys. Chem.* **1996**, *100*, 9116−9126. Luo, Y.; Norman, P.; Macak, P.; Ågren, H. *J. Phys. Chem. A* **2000**, *104*, 4718−4722.

(11) Di Bella, S.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 4440−4445.

(12) Yu, J. W.; Zerner, C. *J. Chem. Phys.* **1994**, *100*, 7487−7494.

(13) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. *J. Am. Chem. Soc.* **1994**, *116*, 10703−10714.

(14) Chen, G.; Lu, D.; Goddard, W. A., III *J. Chem. Phys.* **1994**, *101*, 5860−5864. Lu, D. Q.; Chen, G. H.; Perry, J. W.; Goddard, W. A., III *J. Am. Chem. Soc.* **1994**, *116*, 10679−10685.

(15) Wortmann, R.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 1001−1007.

(16) Thompson, W. H.; Blanchard-Desce, M.; Hynes, J. T. *J. Phys. Chem. A* **1998**, *102*, 7712−7722.

(17) Thompson, W. H.; Blanchard-Desce, M.; Alain, V.; Muller, J.; Fort, A.; Barzoukas, M.; Hynes, J. T. *J. Phys. Chem. A* **1999**, *103*, 3766−3771.

(18) Huang, J. Y.; Lewis, A.; Loew, L. *Biophys. J.* **1988**, *53*, 665−670. Cade, N. A.; Kolinsky, P. V.; Jones, R. J.; Peterson, I. R.; Ahmad, M. M.; Neal, D. B.; Petty, M. C.; Roberts, G. G.; Feast, W. J. *J. Opt. Soc. Am. B* **1987**, *4*, 950−955.

(19) Marder, S. R.; Perry, J. W.; Schaefer, W. P. *Science* **1989**, *245*, 626−628.

(20) Campagnola, P. J.; Wei, M. D.; Lewis, A.; Loew, L. M. *Biophys. J.* **1999**, *77*, 3341−3349.

(21) Braun, D.; Fromherz, P. *Phys. Rev. Lett.* **1998**, *81*, 5241−5244. Moreaux, L.; Sandre, O.; Charpak, S.; Blanchard-Desce, M.; Mertz, J. *Biophys. J.* **2001**, *80*, 1568−1574.

(22) Fromherz, P.; Vetter, T. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 2041−2045.

(23) Bouevitch, O.; Lewis, A.; Pinevsky, I.; Wuskell, J. P.; Loew, L. M. *Biophys. J.* **1993**, *65*, 672−679.

(24) Peleg, G.; Lewis, A.; Linial, M.; Loew, L. M. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 6700−6704.

(25) Fromherz, P. *ChemPhysChem* **2002**, *3*, 276−284.

(26) Fluhler, E.; Burnham, V. G.; Loew, L. M. *Biochemistry* **1985**, *24*, 5749−5755.

(27) Loew, L. M.; Scully, S.; Simpson, L.; Waggoner, A. S. *Nature* **1979**, *281*, 497−499.

(28) Fromherz, P.; Lambacher, A. *Biochim. Biophys. Acta* **1991**, *1068*, 149−156.

(29) Clarke, R. J.; Zouni, A.; Holzwarth, J. F. *Biophys. J.* **1995**, *68*, 1406−1415.

(30) Alain, V.; Blanchard-Desce, M.; Ledoux, I.; Zyss, J. *Chem. Commun.* **2000**, *5*, 353−354.

(31) Benson, H. G.; Murrell, J. N. *J. Chem. Soc., Perkin Trans. 2* **1972**, *68*, 137. Jacques, P. *J. Phys. Chem.* **1986**, *90*, 5535−5539. Morley, J. O.; Morley, R. M.; Docherty, R.; Charlton, M. H. *J. Am. Chem. Soc.* **1997**, *119*, 10192−10202.

(32) Loew, L. M.; Simpson, L.; Hassner, A.; Alexanian, V. *J. Am. Chem. Soc.* **1979**, *101*, 5439−5440.

(33) Hébert, P.; Baldacchino, G.; Gustavsson, T.; Mialocq, J.-C. *J. Photochem. Photobiol. A: Chemistry* **1994**, *84*, 45−55.

(34) Barzoukas, M.; Runser, C.; Fort, A.; Blanchard-Desce, M. *Chem. Phys. Lett.* **1996**, *257*, 531−537.

(35) Castiglioni, C.; Del Zoppo, M.; Zerbi, G. *Phys. Rev. B* **1996**, *53*, 13319−13325.

(36) Bishop, D. M.; Champagne, B.; Kirtman, B. *J. Chem. Phys.* **1998**, *109*, 9987−9994.

(37) Painelli, A.; Terenziani, F. *Chem. Phys. Lett.* **1999**, *312*, 211−220.

(38) Barzoukas, M.; Muller, J.; Fort, A.; Marder S. R.; Alain V.; Blanchard-Desce, M. In *Nonlinear Optical Properties of Organic Materials IX*; Mohlmann, G. R., Ed.; SPIE Proceedings, Vol. 2582, SPIE: Bellingham, WA, 1996.

(39) Blanchard-Desce, M.; Barzoukas, M. *J. Opt. Soc. Am. B* **1998**, *15*, 302−307.

(40) Barzoukas, M.; Blanchard-Desce, M. *J. Chem. Phys.* **2000**, *112*, 2036−2044.

(41) The model developed in refs 16 and 17 has recently been criticized (Boldrini, B.; Cavalli E.; Painelli, A.; Terenziani, F. *J. Phys. Chem. A* **2002**, *106*, 6286−6294). But as will be discussed elsewhere (Laage, D.; Thompson, W. H.; Blanchard-Desce, M.; Hynes, J. T., manuscript in preparation), these criticisms are in fact baseless.

(42) Ephardt, H.; Fromherz, P. *J. Phys. Chem.* **1991**, *95*, 6792−6797. Fromherz, P. *J. Phys. Chem.* **1995**, *99*, 7188−7192.

(43) For some CPPP, the excited-state dynamics may lead to a twisted intramolecular charge transfer (TICT) state (Ephardt, H.; Fromherz, P. *J. Phys. Chem.* **1989**, *93*, 7717−7725. Tatikolov, A. S.; Ponterini, G. *J. Photochem. Photobiol. A: Chem.* **1998**, *117*, 35−41. Cao, X.; Tolbert, R. W.; McHale, J. L.; Edwards, W. D. *J. Phys. Chem. A* **1998**, *102*, 2739−2748. McHale, J. L. *Acc. Chem. Res.* **2001**, *34*, 265−272), but this TICT state is nonfluorescent;[42] thus, the only observed fluorescence is emitted from the same excited state as the Franck−Condon state reached by absorption.

(44) Plaza, P.; Laage, D.; Martin, M. M.; Alain, V.; Blanchard-Desce, M.; Thompson, W. H.; Hynes, J. T. *J. Phys. Chem. A* **2000**, *104*, 2396−2401.

(45) Bayliss, N. S.; McRae, E. G. *J. Phys. Chem.* **1954**, *58*, 1002−1006. McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562−572. McRae, E. G. *Spectrochim. Acta* **1958**, *12*, 192−210. Lippert, E. *Z. Elektrochem.* **1961**, *61*, 962. Liptay, W. *Z. Naturforsch.* **1965**, *20a*, 1441−1471. Liptay, W.; Walz, G. *Z. Naturforsch.* **1971**, *26a*, 2007−2019.

(46) The Kosower Z-value polarity scale (Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253−3260) is based on the solvatochromic behavior of 1-ethyl-4-(carbomethoxy)pyridinium iodide. This salt forms a tight ion-pair complex in solution. While in CPPP the absorption transition corresponds to an intramolecular CT not involving the counterion, the excitation of pyridinium iodide induces an electron transfer (ET) from the iodide anion to the pyridinium ring, resulting in two radicals. Kosower explains the observed blue shift in absorption with increasing solvent polarity by the smaller dipole moment of the excited state compared to the ground state. The details of this explanation have been contested (Larsen, J. W.; Edwards, A. G.; Dobi, P. *J. Am. Chem. Soc.* **1980**, *102*, 6780−6783), but the ET from the iodide anion to the pyridinium ring seems well established because the two resulting radicals have been experimentally detected after excitation (Kosower, E. M.; Lindqvist, L. *Tetrahedron Lett.* **1965**, *50*, 4481−4485). The absorption blue shifts observed for CPPP and pyridinium iodide have qualitatively different origins because for pyridinium iodide it is an equilibrium solvation effect and a blue shift should be observed in emission as well while for CPPP it is a purely nonequilibrium effect and absorption and emission wavelengths shift in opposite directions.

(47) Renge, I. *J. Phys. Chem. A* **2000**, *104*, 7452−7463.

(48) Molecular dynamics simulations of a model polyene in a low and a high polarity solvent were carried out to assess the importance of the counterion.[49] No correlation was found between the polyene−counterion interaction energy and the polyene electronic transition energy.

(49) Laage, D. Ph.D. Thesis, Ecole Normale Supérieure−University Paris VI, Paris, France, 2001.

(50) With eqs 9, 12, and 15, it can be shown that $|\mathrm{MIX}_g/\mathrm{MIX}_{ex}| = (1 + \lambda_s/E_{em})/(1 - \lambda_s/E_{abs}) > 1$, that is, that the mixing of the two valence bond states is always more important in the adiabatic excited state than in the adiabatic ground state.

(51) Another, totally adiabatic, approach can be adopted (see ref 49) and leads to the same results. This approach yields explicit expressions for the adiabatic equilibrium gap and the adiabatic solvent reorganization energies in the ground and excited states.

(52) This can be easily shown for a zero equilibrium diabatic gap, which, for given reorganization energies λ_s and λ_q and given electronic coupling β_c, is the less favorable case to have a single minimum in the adiabatic ground state.

(53) Cannon, R. D. In *Electron-Transfer Reactions*; Butterworth: London, 1980; pp 188−202.

(54) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966−978.

(55) In a cyanine structure, the endgroup charges are identical in the two VB states, the molecule is totally planar, and all of the conjugated bonds in the bridge have the same length.

(56) Sharp, K. A.; Honig, B. *Annu. Rev. Biophys. Biophys. Chem.* **1990**, *19*, 301−332. Davis, M. E.; McCammon, J. A. *Chem. Rev.* **1990**, *90*, 509−521.