Excited-State Dynamics in Polar Solvents of Push−Pull Polyenes Designed for Nonlinear Optics

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Subpicosecond spectroscopy of push−pull polyenes, previously designed to achieve large optical nonlinearities, reveals an isosbestic point in the time-resolved gain band in polar solvents. The compounds possess a diethylthiobarbituric acid electron-withdrawing group and a dibutylaniline electron-releasing group coupled by a π-conjugated chain. The final gain peak exhibits a regular red shift with increasing chain length, whereas the ground-state absorption shift levels off. A fast photoinduced process toward a rigid, fully conjugated cyanine-like structure is proposed. This observation supports a recent proposal that a proper description of the excited-state dynamics of these push−pull polyenes requires more than two valence bond states.

1. Introduction

Push−pull polyene systems, characterized by electron donor (D) and acceptor (A) groups separated by a π-conjugated chain, have received extensive recent attention in connection with their nonlinear optical (NLO) properties, e.g., large hyperpolarizabilities.[1−11] One major interpretive mode for the NLO properties for this molecular class and a helpful guide in designing molecules with tailored NLO properties has been a two valence bond state description,[3−6] to which the Goddard group has made important initial contributions.[3] In the present work, subpicosecond spectroscopy is applied to a novel class of push−pull polyenes in order to directly probe the validity of this simplified description.

These push−pull polyenes, with a dibutylaniline end group (D) and a diethylthiobarbituric acid end group (A) linked by a chain of increasing length (Chart 1, $n = 2−5$), have been designed and characterized as efficient nonlinear optical chromophores with giant quadratic hyperpolarizabilities ($\beta(0)$ up to 1000×10^{-30} esu).[12,13] The estimated permanent dipole moment change $\Delta\mu$ upon S_0-S_1 excitation is as large as 42 D for the longest chain ($n = 5$).

The theoretical model[3−6] that guided the design of these compounds describes the ground-state S_0 and excited-state S_1 as a mixing of two limiting resonance forms (two valence bond (VB) states): neutral (D−A) and zwitterionic (D$^{\partial+}$−A$^{\partial-}$) and relates the NLO properties and the degree of ground-state zwitterionic character. The zwitterionic state required by this model is not necessarily the one obtained by transferring one full electron from the donor to the acceptor. Indeed a partial ionization is indicated, as the dipole moments associated with the zwitterionic state obviously show.[5,6,14] An improved model recently proposed[14] and applied[14,15] within this framework

CHART 1

$n = 2$ to 5
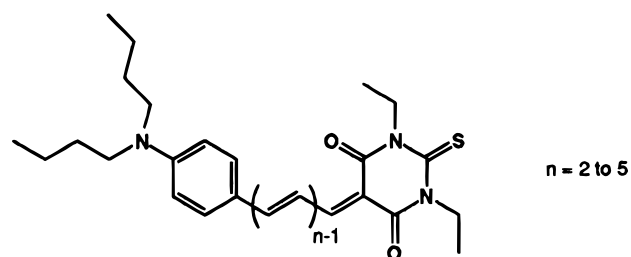
includes (a) the polar solvent effect on the ground-state charge-transfer character as well as nonequilibrium solvation on the Franck−Condon excited state and (b) a bond length alternation (BLA) coordinate[2−7] gauging the bonding geometry pattern in the π-conjugated chain. It was also suggested,[14] on the basis of a number of considerations,[14,15] that a description involving more than two VB states may be required and that the study of the excited-state dynamics would be a valuable test of this issue. We note in passing that the two VB state model has been criticized[16] on other grounds, involving the relation between vibrational and electronic (hyper)polarizabilities.[4,16−20]

In brief, the ground and excited electronic adiabatic states are represented by the two free energy surfaces

$$G_{e,g}(q,s) = \frac{G_N(q,s) + G_Z(q,s)}{2} \pm \frac{1}{2}\sqrt{[G_Z(q,s) - G_N(q,s)]^2 + 4t^2} \quad (1)$$

as a function of the BLA coordinate q and a solvent coordinate s, which is a measure of the solvent orientational polarization.[14]
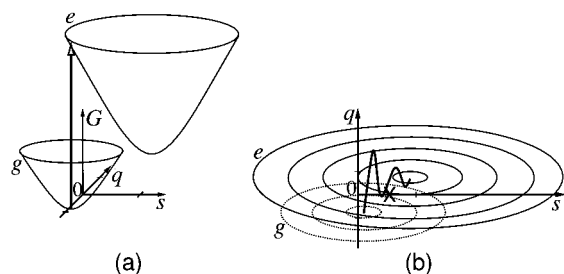
Figure 1. (a) Schematic illustration of two VB state model[14] ground (g) and excited (e) adiabatic free energy surfaces in vibrational (q) and solvent (s) coordinates with the Franck–Condon transition indicated. The indicated q axis points correspond to the antisymmetrically related equilibrium values of q for the limiting neutral and zwitterionic VB states, while the origin and the indicated point on the s axis correspond to equilibrium solvation values for those two VB states. (b) Corresponding contour plots, with an example relaxation trajectory that reflects the significant difference in the force constants for the two coordinates. The cyanine configuration is indicated by X.

Here, G_N and G_Z are respectively the free energy surfaces of the diabatic electronic neutral (N) and zwitterionic (Z) VB states, and t is the electronic resonance coupling that mixes the two VB forms such that the ground- and excited-state wave functions are

$$\Psi_{g,e} = c_N^{g,e}\psi_N + c_Z^{g,e}\psi_Z \tag{2}$$

where the q- and s-dependent coefficients $c_N^{g,e}$ and $c_Z^{g,e}$ govern the weights of the VB forms ψ_N and ψ_Z in the two electronic states. The VB free energy surfaces are quadratic functions in each of the two coordinates, with appropriate force constants for the respective displacements.[14] For the push–pull polyene molecules to be discussed below, it has been found[14,15] from the model that at their respective equilibrium values of q and s the ground state has a single minimum and is largely neutral, $c_N^g \gg c_Z^g$, while the excited state also has a single minimum and is largely zwitterionic, $c_Z^e \gg c_N^e$. Equivalently stated, the equilibrium values of the q and s coordinates in the ground state are close to those of the pure neutral VB state, while the q and s equilibrium values in the excited state are close to those of the pure zwitterionic VB state.

The spectroscopic situation is illustrated in Figure 1, which represents the model ground- and excited-state surfaces (eq 1) as a function of the solvent and the BLA configurational coordinates for the molecular class studied here. The two VB state model predicts a simple time-dependent emission (fluorescence or gain) Stokes shift due to solvation and BLA configurational dynamics within a *single* excited electronic state when the molecule is optically excited from the relaxed (mainly neutral) ground state to the nonequilibrated highly polar (mainly zwitterionic) excited state. In contrast to this simple behavior, a more complex spectral dynamics would result if additional VB states are required in the description.[14]

To check the two VB state model's validity and to bring insight into the short time photoinduced excited-state dynamics and properties of these compounds, we have carried out time-resolved spectroscopy experiments of the $n = 2-5$ polyenes (PA2 to PA5) with subpicosecond resolution. To help discriminate between intramolecular and solvent dynamics, we chose dioxane, tetrahydrofuran, and acetonitrile as solvents. The average solvation times of these solvents[21] are close to or less than the time-resolution of our pump–probe setup (~1 ps). This excludes solvation dynamics from the accessible scope of the present experimental study; within the two VB state description,

this also implies that any dynamics observed would have to be BLA configurational relaxation within the single excited electronic state, provided it is slower than about 1 ps.

2. Experimental Section

Differential absorption spectra were measured by the pump–probe technique using ~0.5 ps, 10–20 μJ pump pulses around 573 or 610 nm and a white-light continuum probe produced by focusing ~200 μJ of the same laser beam in a 1 cm D_2O cell. The pump–probe experiments were carried out with a two-beam probe arrangement; one beam is sent to the sample and the other used as reference. The path of the sample cell was 1 mm long. The pump and probe beams had a diameter of about 1 mm on the sample and crossed at an angle of ~10°. The transmitted probe beams were then guided through optical fibers to the entrance slit of a polychromator (Spex 270 M). The two probe beam spectra were simultaneously recorded by a computer-controlled double-diode array detector (Princeton Instrument Inc. DDA-512). The pump–probe delay time was adjusted via a stepper motor translation. Pump and probe beam polarizations were set at the magic angle. Data were accumulated over 500 or 1000 laser shots.

The ~573 and ~610 nm subpicosecond pulses were provided by an unconventional dye laser.[22] The whole system is driven by a single seeded 10 Hz Q-switched Nd:YAG laser delivering smooth 6 ns pulses at 532 nm. The 500 fs pulses at ~610 nm are produced and used either directly in the pump–probe setup or to generate a continuum that is filtered at ~573 nm and further amplified in a rhodamine 6G amplifier chain pumped by the same Nd:YAG laser.

The design, preparation, and purification procedures of the push–pull polyenes were reported elsewhere.[12] Their all-trans configuration was characterized by ^{1}H NMR studies.[12] Identification of all vinylic protons was achieved by performing COSY experiments at 400 MHz. This allowed for the determination of ^{1}H–^{1}H coupling constants between vicinal vinylic protons in the polyenic chain and provided evidence of the all-trans configuration of the push–pull polyenes studied in the present work. In addition, AM1 semiempirical calculations[12] gave further information about the structure and conformation of the push–pull polyenes; these calculations yield planar conjugated polyenic chains with an extended zigzag conformation. Dioxane, tetrahydrofuran, and acetonitrile solvents were of UV spectroscopy grade (Merck, Uvasol). The solutions (not deaerated) were used immediately after preparation or kept in the freezer (−27 °C). The absorption and fluorescence spectra were checked respectively with a Cary 210 spectrophotometer and a Quanta-Master 1 PTI spectrofluorometer. The fluorescence measurements were limited to wavelengths below 800 nm. In pump–probe experiments, the solute concentration was fixed to have an optical density between 0.3 and 1 at the excitation wavelength; solutions were recirculated so that the excited volume was renewed at each pump pulse. The experiments were carried out at room temperature.

3. Results

3.1. Time-Resolved Spectra. The early bleaching and gain spectra (ΔD) of PA2 in dioxane are shown in Figure 2. The unexcited sample absorption (D_0) and normalized fluorescence spectra recorded in steady-state experiments are also shown. Within 10 ps after excitation, the time-resolved spectra exhibit one temporary isosbestic point (TIP) around 608 nm where the gain is dominant ($\Delta D < 0$, $D_0 \approx 0.1$), with a large signal decay around 580 nm and large rise around 620 nm and above.
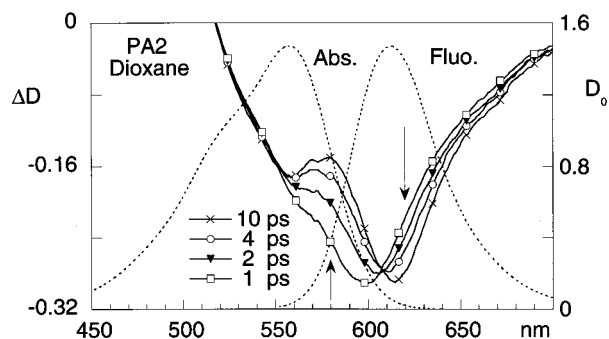
Figure 2. Transient bleaching and gain spectra (ΔD, left scale) of PA2 in dioxane within 10 ps after excitation with a 500 fs laser pulse at 572 nm. Absorption spectrum of the unexcited sample (Abs, D_0 right scale). Normalized fluorescence spectrum recorded in steady-state experiments (Fluo).
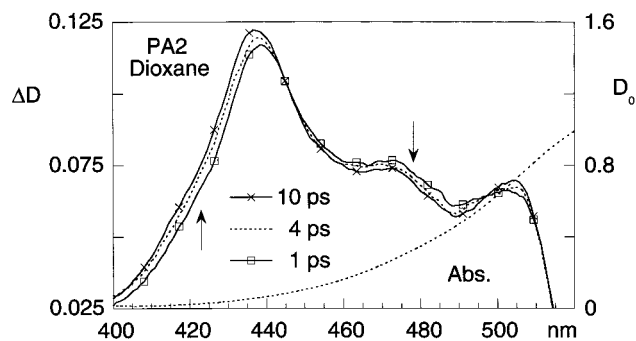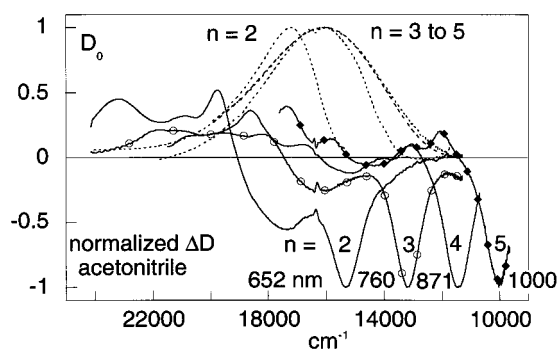

Figure 3. Transient absorption spectra (ΔD, left scale) of PA2 in dioxane within 10 ps after excitation with a 500 fs laser pulse at 572 nm. Unexcited sample absorption spectrum (Abs, D_0 right scale).
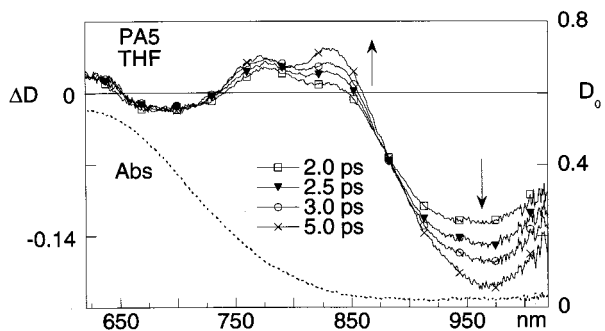
Figure 4. Transient spectra (ΔD, left scale) of PA5 in tetrahydrofuran within 5 ps after excitation with a 500 fs laser pulse at 610 nm. Unexcited sample absorption spectrum (Abs, D_0 right scale).

Another TIP is observed around 450 nm in the transient absorption band with smaller amplitude signal changes (Figure 3). The TIP in the gain band is seen for all polyenes (PA2 to PA5) in dioxane and tetrahydrofuran. For example, the time-resolved spectra measured within 5 ps after excitation of PA5 in tetrahydrofuran are shown in Figure 4; the final gain band has a maximum around 970 nm (the corresponding fluorescence spectrum could not be measured in this wavelength range). The TIP in the transient absorption band is observed for PA2 and PA3 but not for PA4 and PA5, which only show shape changes, delayed increase, and/or shift. In acetonitrile, the most polar solvent used, the transient spectra exhibit a retarded rise with a slight red shift of the gain band, concomitant with slight changes in shape of the transient absorption band, but no TIP can be observed except for PA5. These spectral changes are not observed in a nonpolar solvent such as cyclohexane.

In a given polar solvent, once this initial fast spectral evolution is finished, the transient spectra exhibit a narrow gain band,

Figure 5. Normalized ground-state absorption spectra (D) and transient absorption/bleaching/gain spectra (ΔD) measured at a few picoseconds after excitation of PA2, PA3, PA4, and PA5 solutions in acetonitrile with a 500 fs laser pulse at 610 nm.

with a regular red shift from PA2 to PA5. Figure 5 shows the normalized transient absorption/gain spectra, measured at a few picoseconds pump–probe delays, and the corresponding normalized ground-state absorption spectra in acetonitrile. The positions of the maxima of the gain band and of the ground-state absorption are given in Table 1. In all solvents, the gain peak (λ_{gain}) shifts by ~100 nm per added double bond in the conjugated chain, whereas the ground-state absorption peak (λ_{abs}) shows saturation of the shift and broadening (Figure 5).

3.2. Kinetics. We have fit the $\Delta D(t)$ kinetics of PA2 to PA5 up to 1.6 ns, in dioxane, tetrahydrofuran and acetonitrile, with a biexponential function plus a constant (simulating a very long-lived exponential) convoluted with a Gaussian function. In some cases a three-exponential fit was necessary. The fwhm of the Gaussian function, i.e., the pump–probe cross-correlation time, was generally fit as 1.1 ± 0.3 ps. Only the short time component τ_1, i.e., the initial fast rise or decay of $\Delta D(t)$, is given in Table 1 at selected probe wavelengths (λ_p) for an excitation wavelength λ_{exc}. The rightmost column of Table 1 corresponds to the probe spectral range where the gain is dominant; in some other cases, the bleaching contributes to the observed signal. For each push–pull polyene in the three solvents, τ_1 depends little on the probe wavelength within experimental error, except in the spectral blue edge where some long components (i.e., $10-17$ ps) appear in the transient absorption signal rise. For PA2 in acetonitrile where the data are compared for two excitation wavelengths, this long component disappears when the excitation wavelength is tuned from 573 to 609 nm. Neglecting these long time components, one observes that τ_1 depends little on the chain length for PA2 to PA4 but is solvent-dependent. The average time constant decreases with increasing solvent dielectric constant, from 2.6 ps in dioxane to 1.8 ps in tetrahydrofuran to 1.1 ps in acetonitrile. For PA5, the time constant is roughly 2 ps in the three solvents. For simplicity, we used the dielectric constant (see Table 1) to characterize solvent polarity. It is nevertheless known that microscoscopic solvation properties of the nondipolar solvent dioxane are not directly reflected by its macroscopic dielectric properties[23] and that empirical solvent polarity parameters such as π^* [24] and E_T^N [25] indicate that its polarity is in fact close to that of tetrahydrofuran.

4. Discussion

The presence of temporary isosbestic points (TIP) in the time-resolved spectra indicates that a reaction occurs in the excited push–pull polyenes, with a precursor–successor relationship between the initially prepared excited-state population and that of a product species, without a change in the total population.

Dynamics of Polyenes

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TABLE 1: Spectral and Kinetic Data of PA2 to PA5 Push−Pull Polyenes in Three Solvents of Increasing Dielectric Constant (ϵ): Dioxane, Tetrahydrofuran, and Acetonitrile[a]

PAn	λ_{abs} (nm)	λ_{gain} (nm)	λ_{exc} (nm)	λ_p (nm)	τ_1 (ps)	λ_p (nm)	τ_1 (ps)	$\lambda_{p\ gain}$ (nm)	τ_1 (ps)
					Dioxane (ϵ = 2.21 at 25 °C)[53]				
PA2	558	616	572	429	17* ± 6	586[b]	2.5 ± 0.2	614	2.9* ± 0.5
				484[b]	2.7 ± 1.0	558[b]	1.4 ± 0.2	660	3.3* ± 0.5
PA3	583	718	609	512[b]	10 ± 3	595[b]	1.7 ± 3		
						650[b]	2.4 ± 0.2	761	3.2* ± 1.2
PA4	599	834	573	525[b]	2.4* ± 0.4	630[b]		823	3.2* ± 0.5
				536[b]	1.1* ± 0.2	712[b]w	4.4 ± 0.4	845	2.3* ± 0.4
PA5	608	955	573	583[b]	1.8* ± 0.2	770 w	2.0* ± 0.3	925 w	1.8* ± 0.2
				616[b]	3.1 ± 0.4			958 w	1.3* ± 0.2
					Tetrahydrofuran (ϵ = 7.6 at 25 °C)[53]				
PA2	571	640	609	477[b] w	1.1 ± 0.4	600[b]	1.9 ± 0.1	660	1.4* ± 0.4
PA3	605	746	610	460	2.2* ± 0.4	638[b]	2.4 ± 1.0	745	1.6* ± 0.5
				494[b]	1.3 ± 0.3	671[b]	1.9 ± 0.2	782	2.3* ± 1.1
PA4	621	853	610	543[b]	17* ± 11	653 w	1.9* ± 2.5	829	2.2* ± 0.7
				589[b] w	2.1* ± 1.6	764 w	2.15 ± 0.2	856	2.3* ± 0.3
PA5	624	970	610	574[b]	2.9* ± 1.0	772[b] w	1.05* ± 0.2	970	1.6* ± 0.17
				579[b]	1.4 ± 0.4	841 w	1.6* ± 0.1	998	1.7* ± 0.14
					Acetonitrile (ϵ = 37.5 at 20 °C)[53]				
PA2	580	652	573	429	16* ± 3	558[b]	4.6* ± 0.8	651	0.7* ± 0.3
				503[b]	11* ± 2	613[b]	1.2 ± 0.8	668	0.9* ± 0.1
			609	429		558[b]		641	1.4* ± 0.4
				503[b]		613[b]	1.4 ± 0.3	669	0.6* ± 0.2
PA3	618	760	609	449	5* ± 5	643[b]	2 ± 1	763	0.6* ± 0.2
				551[b]	0.9* ± 0.6	698[b]	1.1 ± 0.3	790	0.8* ± 0.2
PA4	624	871	610	484	1 ± 3	667[b] w	1.7 ± 0.7	835	1.1 ± 0.3
				600[b] w	1.0* ± 0.1	761[b] w	1.0* ± 0.1	900	0.9* ± 0.8
PA5	623	1000	610	577[b]	9.4* ± 2.4	825[b]	3.8* ± 0.7	990	2.1* ± 0.3
				632[b]	9* ± 2	834	2.1* ± 0.4	1000	1.2* ± 0.1

[a] Maximum of ground-state absorption (λ_{abs}). Maximum of gain band (λ_{gain}) measured a few picoseconds after excitation at wavelength λ_{exc} with a 500 fs laser pulse. Short time components τ_1 obtained from fit of time-resolved differential absorption $\Delta D(t)$ at various probe wavelengths (λ_p). *: rise time. $\lambda_{p\ gain}$: gain is dominant. b: bleaching contribution. w: weak signal, $\Delta D < 0.05$.

In the hypothesis of a reaction occurring on an adiabatic surface, this would indicate that the reaction is (at least slightly) barrier-activated; a barrierless path would instead lead to a continuous spectral shift without TIP. Alternatively, a barrierless or low barrier electronically nonadiabatic state interconversion could be involved. That a TIP occurs in the gain band (see Figures 2 and 4) means that both the initially excited state and the product state are emissive.[26] Figure 2 shows that the shape of the final gain band of PA2 in dioxane, with a maximum around 616 nm, is similar to the steady-state fluorescence spectrum, which can thus be attributed to the product state. That the final gain peak regularly shifts when the conjugated chain length increases (n = 2−5), while the ground-state absorption peak shows a saturation of the shift and a broadening (Figure 5), confirms that the absorption and the emission do not involve the same electronic states. In acetonitrile, i.e., at the highest polarity, the nonobservation of a clear TIP for PA2 to PA4 implies that either (a) a TIP exists but cannot be observed because the reaction time (estimated as ~1 ps) is too close to the time resolution of the experiments or (b) there is no TIP, which, in the above-mentioned adiabatic reaction hypothesis, indicates an activationless reaction path.

The present results give unambiguous evidence for an excited-state dynamics not expected from the simple two VB state model[14] and indeed for any description involving a ground and single excited electronic state.[1−13] As emphasized in Introduction, only single-state simple relaxation dynamics, and not reaction dynamics, can result from the two VB state description. We now discuss possibilities for the character of the excited-state reaction process.

The reaction process involves a transient emissive product. It is thus quite different from the trans−cis isomerization reaction known in stilbenes,[27] polyenes,[28−30] and cyanine dyes[30,31] and, as described in detail elsewhere,[32] observed and characterized for some of the present compounds in nonpolar cyclohexane. On the other hand, identification with the $1B_u \rightarrow 2A_g$ internal conversion, which occurs in a variety of linear polyenes[28,29,33,34] and carotenoids,[35] seems very unlikely, since both absorption and fluorescence transitions are highly allowed (large cross sections), indicating that no involved excited state bears A_g state characteristics, i.e., doubly excited electronic configuration with essentially forbidden transition to the ground state. In addition, even if a $2A_g$ state were lower in energy than the optically accessed $1B_u$ state, typical $1B_u \rightarrow 2A_g$ conversion times are very short, about several hundred femtoseconds.[35,36] Further, one would expect any "ionic" $1B_u$ state to be stabilized more than a "covalent" $2A_g$ state in a polar environment[28,29,36−38] such that $2A_g$ could not be a thermodynamically favored excited-state product.

A different idea is that the reaction is of the type reported for electron donor−acceptor compounds such as push−pull stilbene derivatives or merocyanine dyes for which a TIP was observed in the time-resolved fluorescence[39] or gain spectra.[26,40] For these and for push−pull diphenyl polyenes,[41] a photoinduced mechanism involving the fast formation of an emissive intramolecular charge transfer (ICT) state was proposed.[26,39−43] Indeed, the observation that the reaction does not occur in cyclohexane and that, except for PA5, the reaction rate increases with solvent polarity leads us to propose that in polar solvents the probed reaction is of ICT type. Possibilities include a barrier-activated ICT process such as an outer-sphere Marcus-type electron transfer with a solvent-dependent barrier[44,45] or more likely (see below) an ICT process involving an intramolecular coordinate whose barrier may be solvent-influenced and whose reaction

coordinate may involve a solvent component.[41−43,46,47] Neither possibility is excluded by the observation that the reaction times of 2.6 ps in dioxane, 1.8 ps in tetrahydrofuran, and 1.1 ps in acetonitrile are larger than the average solvation times, respectively being 1.7, 0.94, and 0.26 ps.[21] On the other hand, for PA5, since the reaction time (2 ps) is solvent-independent, evidently only an intramolecular coordinate could be invoked. As for the 10−17 ps component observed in the transient absorption blue edge, it depends on the excitation wavelength (Table 1) and may result from excited-state vibrational cooling[48] when the molecule is excited with excess energy.

While the reaction's precise character is unclear, the present results shed some light on the reaction product's character. Returning to Figure 5, it is to be noted that although the gain peak may be shifted from that of fluorescence due to some overlap with the excited-state absorption (particularly for the long chain compounds where transient absorption is seen on the blue edge of the gain band (Figure 4)), a red shift of the gain peak of ∼100 nm per added double bond in the chain indicates that the product state has a cyanine character.[49] This shift is well-known for symmetrical polymethine cyanine dyes.[30,49] The regular shift of the $S_1 \rightarrow S_n$ transient absorption also agrees with this attribution.[50] In two VB state language, the cyanine structure corresponds formally to a 50%−50% mixture of the neutral VB and zwitterionic VB forms (cf. the discussion below eq 2), with a full chain conjugation, no bond length alternation, and a planar rigid geometry. Emission from such a product structure should be solvent-independent (since the ground-state VB composition is the same, differing only in phase), and indeed little solvent dependence is observed (500−900 cm^{-1} from dioxane to acetonitrile (Table 1)). However, production of such a cyanine-like product, which would be presumably less polar than the Franck−Condon state accessed in absorption (which would be essentially the zwitterionic VB state in the two VB state perspective), seems inconsistent with the observation that the reaction is promoted and accelerated by a polar environment; the latter would be more consistent with an FC excited state less polar than the product. In any event, it must be emphasized that in the two VB state description such a cyanine-like product state could never be reached after absorption by simple relaxation in the solvent and configurational coordinates, as Figure 1 makes clear.

5. Conclusion

The picosecond time-resolved spectra measured for four members of a new family of push−pull polyenes give evidence for a fast photoinduced reaction in polar solvents. The reaction time decreases with solvent polarity increase, from 2.6 ps in dioxane to 1.8 ps in tetrahydrofuran to 1.1 ps in acetonitrile, independently of the conjugated chain length from two to four double bonds. A reaction time of about 2 ps is found for the chain with five double bonds in the three solvents. Moreover, the transient species' gain spectra exhibit a regular 100 nm shift when the chain length increases. An intramolecular charge transfer with geometrical change toward the formation of a transient state with a rigid, fully conjugated cyanine-like structure is suggested as a possible explanation of these results. The present study has shown that a simple two valence bond state model, while being extremely useful in the design of push−pull polyenes with optimized nonlinear optical properties and which has had a measure of success in the qualitative prediction of solvent effects on these properties, is completely unable to describe the observed excited-state dynamics of these molecules. These results support the proposal that more than two valence

bond states should be involved in a proper description of the excited-state dynamics;[14,15] work to develop such a description, possibly including additional geometric coordinates as well as additional VB states along the lines discussed earlier by the Goddard group,[3a] is underway. The results of such an improved description could be employed to examine the consequences for NLO properties, the origin of the present work. The precise impact on the NLO properties is not a priori clear, since those properties depend on the Franck−Condon absorption from the ground state and since the influence of the additional state(s) indicated by the present experiments in that region needs to be assessed. Beyond this, the present considerations may also be of interest in connection with other nonlinear spectroscopic processes that involve excited-state absorption and in which excited-state dynamics play a significant role. This includes, for example, reversed saturated absorption and, more generally, multiphoton absorption, which are of particular interest for applications connected with molecular optical-limiting properties.[51,52]

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