

Picosecond Structural Relaxation of Abietic Acid Based Amine End Capped *Para*-Phenylenevinylene Trimers in Solution

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The synthesis and photophysical properties of six new abietic acid based amine end-capped *p*-phenylenevinylene trimers (AECPV3) in their lowest excited singlet states are presented. The AECPV3 compounds show a large red-shift of both the absorption (25–30 nm) and emission (37–42 nm) maxima with respect to those of the corresponding trimers. Picosecond time-resolved

fluorescence data reveal the presence of a fast conformational relaxation process (40–62 ps) of the initially excited compounds, leading to more planar conformers. The conformational relaxation time is proportional to the volume of both the side chain and the amine groups.

Introduction

Electroluminescent (EL) polymers have been extensively investigated over the past twenty years, and light emitting devices (LED) based on conjugated organic polymers have now achieved performances compatible with commercial application.^[1] Poly(*p*-phenylenevinylene) (PPV) is one of the best studied cases due to its excellent luminescent and mechanical properties.^[2] In order to improve the electroluminescence efficiency of PPVs, transport rates of electrons and holes in the emissive layer of EL devices must be enhanced and balanced.

The imbalance of the electron and hole currents, as a consequence of differences in charge mobility, is one of the most important problems in the development of high efficiency LEDs.^[3] One way to optimize the properties of PPVs is to modify the structure with the introduction of end-groups,^[4] acting as hole-trapping (HTM) or electron-blocking molecules. Aromatic amines play this role efficiently by decreasing the mobility of the positive charge carriers, and also reducing the electric field difference between the anode and cathode.^[5,6] In addition, they frequently increase the chemical stability of these systems.

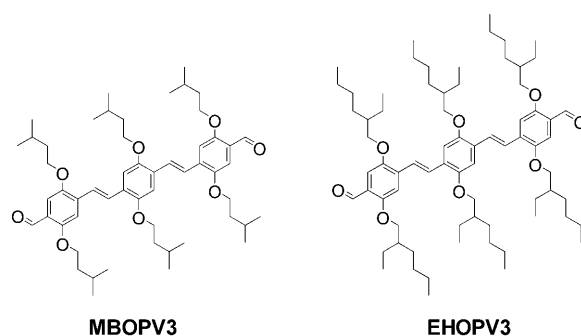
However, amine end-capped polymers may show photophysical processes that are absent in the polymer, such as intramolecular electron and/or energy transfer from the amine to the polymer backbone. There is little information on this issue, and thus a clear need for a detailed photophysical analysis of this class of compounds. Such an analysis may be complex because excited conjugated polymers already show multi-exponential decays with fast (ps) components in film and solution.^[7,8]

We have recently shown the advantages of using dehydroabietic acid based amines in terms of their solution processibility, charge transport and film stability.^[9,10]

Herein, we report the synthesis and the photophysical properties of six new dehydroabietic acid based amine end-capped

derivatives of two *p*-phenylenevinylene trimers (MBOPV3 and EHOPV3).

The photophysical study of MBOPV3 and EHOPV3^[11] has shown that fast conformational relaxation occurs during the early times after excitation (10–100 ps), leading to an increase in the backbone planarization and consequently to a higher



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level of π -delocalization. The rate constant of conformational relaxation k_{CR} decreases both with the size of the side chain and solvent viscosity. It was also found that k_{CR} follows the empirical relationship $k_{CR} = a\eta_0^{-\alpha} \exp(-\alpha E_{\eta}/RT)$, where $a\eta_0^{-\alpha}$ is the frequency factor, η_0 is the pre-exponential coefficient of viscosity, E_{η} is the activation energy of viscous flow and α is an empirical parameter relating the solvent microscopic friction involved in the conformational change to the macroscopic solvent friction ($\alpha = 1$).

It is shown in this work that the end-capped *p*-phenylenevinylene trimers (AECPV3) constitute a useful model system in two ways: 1) to understand how the end-capped amine system couples to the conjugated polymer with respect to orbital delocalization, energy and/or electron transfer, and 2) to investigate how side-chains and end-groups affect conformational relaxation.

Results and Discussion

Synthesis

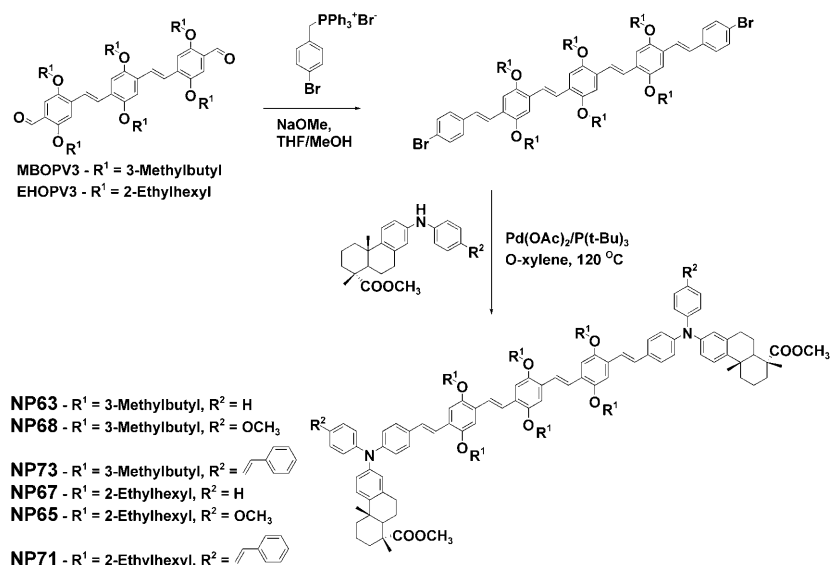
The synthesis of the dehydroabietic acid based triarylamine end-capped *p*-phenylenevinylene trimers (AECPV3) was carried out by a two step procedure as depicted in Scheme 1.

In the first step, a Wittig condensation was chosen, where the terminal formyl groups of the MBOPV3 and EHOPV3 reacted with a phosphonium salt, 4-bromobenzyl triphenylphosphonium bromide, to obtain the terminal bromophenyl derivatives BPMBOPV3 and BPEHOPV3.^[12] Next, these arylbromide derivatives reacted with three diarylamines from dehydroabietic acid by a palladium cross-coupling reaction^[13] to obtain in good yields six new end-capped triarylamine OPVs, here named AECPV3 (NP63, NP65, NP67, NP68, NP71 and NP73). The new compounds, diarylamines, arylbromide intermediates as well as the end-products, were characterized by FTIR, NMR, mass spectrometry and/or elemental analysis.

Absorption and Fluorescence Spectra

Figure 1 shows absorption and fluorescence spectra of the amine- end-capped trimers (AECPV3) in toluene at 293 K.

The absorption spectra are red-shifted 25–30 nm with respect to the trimers MBOPV3 and EHOPV3 (Table 1). The absorption spectra of both styryl–phenyl AECPV3s (NP71 and NP73) show a band at 379 nm, which is similar to the absorp-



Scheme 1. Synthesis of the dehydroabietic acid based triarylamine end-capped *p*-phenylenevinylene trimers (AECPV3).

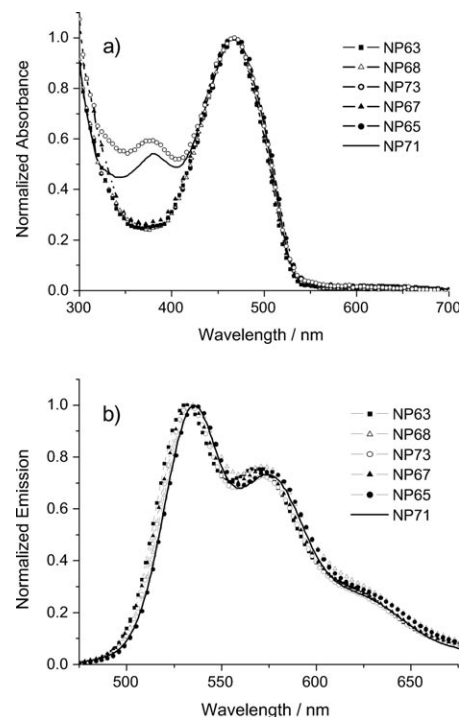


Figure 1. Normalised steady-state absorption (a) and fluorescence spectra (b) of AECPV3 in toluene, at 293 K. The emission spectra were obtained with excitation at 467 nm. The absorption and fluorescence maxima wavelength values can be found in Table 1.

tion of the corresponding styryl–phenyl amine (see Figure 2 and text related with this figure).

The fluorescence spectra exhibit vibrational structure similar to that show by the trimers^[14] and the related MEH-PPV polymer.^[15] Slight differences in the emission wavelength can be

Table 1. Absorption (λ_{abs}) and emission (λ_{em}) wavelength maxima, fluorescence quantum yields (ϕ_{F}), lifetimes (τ_{F}) and radiative (k_{F}) and radiationless (k_{NR}) rate constants of the AECPV3s in toluene at 293 K.

Compound	λ_{abs} [nm]	λ_{em} [nm]	ϕ_{F}	τ_{F} [ns] ^[a]	k_{F} [ns ⁻¹]	k_{NR} [ns ⁻¹]
MBOPV3	438 ^[11]	493 ^[11]	0.72 ^[14]	1.54 ^[11]	0.47	0.18
NP63	465	532	0.57	0.76	0.75	0.57
NP68	468	535	0.58	0.79	0.73	0.53
NP73	468	533	0.56	0.77	0.72	0.57
EHOPV3	440 ^[11]	496 ^[11]	0.71 ^[14]	1.54 ^[11]	0.46	0.19
NP67	465	533	0.57	0.76	0.75	0.57
NP65	469	537	0.56	0.78	0.72	0.57
NP71	468	536	0.57	0.77	0.74	0.56

[a] Major component (>90%) from triexponential decays (see Figure 3 and Table 2)

observed, with the methoxy-phenyl AECPV3 derivatives (NP68 and NP65) being those showing the most red-shifted spectra (Table 1).

Fluorescence quantum yields of the AECPV3 compounds, in toluene at 293 K, are slightly lower than those of the parent trimers and display similar values within the experimental error (0.57 ± 0.01). Using the major lifetime of the AECPV3, the values of the radiative and the sum of the radiationless rate constants are all similar ($k_{\text{F}} = \Phi_{\text{F}}/\tau_{\text{F}} = 7.4 \times 10^8 \text{ s}^{-1}$ and $k_{\text{NR}} = (1 - \Phi_{\text{F}})/\tau_{\text{F}} = 5.6 \times 10^8 \text{ s}^{-1}$, respectively). These values are both larger than those of the parent trimers.

Absorption and emission spectra of the individual amines in methylcyclohexane (MCH) at 293 K are shown in Figure 2. The absorption spectrum of the abietic acid based amine containing the styryl-phenyl group shows the first absorption band with maximum at 370 nm, which is not present in the absorption spectra of the two other amines. The other absorption band at 297 nm is common to the three amines. Only the abietic acid based amine containing the styryl-phenyl group shows fluorescence.

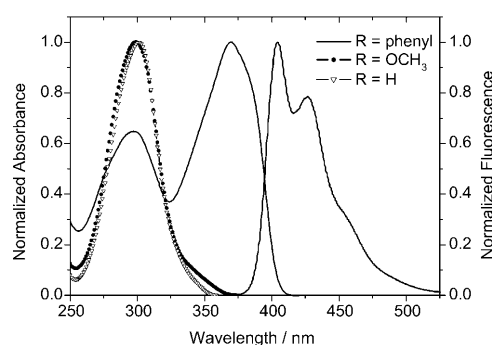


Figure 2. Normalized absorption spectra of the amines used as end-groups in the AECPV3 studied, in MCH at 293 K, and the fluorescence spectrum of the styryl-phenyl amine, with excitation at 370 nm.

Fluorescence Decays (Excitation at 440 nm)

Fluorescence decays of AECPV3 in toluene at 293 K, were measured under identical conditions, with 6.128 ps/channel and

$\lambda_{\text{exc}} = 440 \text{ nm}$, at three emission wavelengths: 510 nm (the onset of the emission band), 560 nm and 610 nm (the tail of the emission band). With this time resolution, all decays can only be fitted with triple exponential functions showing two major components τ_3 and τ_2 and a third residual component τ_1 , due to an impurity (see forthcoming discussion). Figure 3 shows the fluorescence decays obtained for the AECPV3 NP68.

The values of the three decay times obtained from independent analysis at each wavelength do not show any significant change along the fluorescence spectrum and can be considered as independent of the emission wavelength. This allows a global analysis of the fluorescence temporal profiles. The decay times and pre-exponential coefficients obtained from the global analysis for each one of the AECPV3, collecting at 6.128 ps/channel, are shown in Table 2.

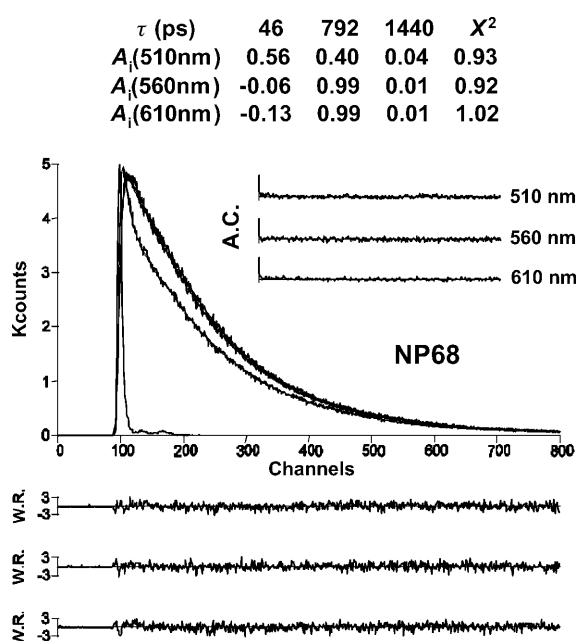


Figure 3. Global fits of the fluorescence decays for NP68 in toluene at 293 K, measured with excitation at 440 nm and emission at 510, 560 and 610 nm with 6.128 ps/channel. The decay times and pre-exponential coefficients at each wavelength resulting from the fits are shown above. Also shown are the weighted residuals (W.R.), autocorrelation functions (A.C.), the χ^2 values and pulse profile (FWHM = 19 ps).

The values of the pre-exponential coefficient (a_3) of the shortest lifetime component are positive at 510 nm, and become negative at 610 nm, meaning that a population of molecules emitting at shorter wavelengths (band onset) is being converted into a population emitting at longer wavelengths (tail). In the case of the corresponding non-end-capped oligomers (MBOPV3 and EHOPV3), the fast components (τ_3) also appear as decay-time at the onset of the emission spectrum and as rise time at longer wavelength.^[11]

The intermediate component (τ_2) has similar values for all the AECPV3 studied in this work (760–790 ps), and represents the largest contribution to the fluorescence decay at all emis-

Table 2. Fluorescence decay times (τ_i) and pre-exponential coefficients (a_i) resulting from global triexponential fits of the decays of end-capped PV trimers in toluene at 293 K, measured at three emission wavelengths with excitation at 440 nm.

	τ_3 [ps]	τ_2 [ps]	τ_1 [ps]	510 nm			560 nm			610 nm		
				a_3	a_2	a_1	a_3	a_2	a_1	a_3	a_2	a_1
NP63	40	759	1430	0.41	0.55	0.04	-0.02	0.96	0.04	-0.17	0.97	0.03
NP68	46	792	1440	0.56	0.40	0.04	-0.06	0.99	0.01	-0.12	0.99	0.01
NP73	52	774	1440	0.44	0.54	0.02	0.03	0.95	0.02	-0.12	0.98	0.02
NP67	53	761	1340	0.44	0.52	0.04	0.07	0.90	0.03	-0.07	0.97	0.03
NP65	55	778	1260	0.51	0.46	0.03	0.05	0.92	0.03	-0.13	0.96	0.04
NP71	62	768	1330	0.48	0.49	0.03	0.04	0.93	0.03	-0.11	0.97	0.03

sion wavelengths studied. In fact, this contribution to the total fluorescence intensity ($I_F = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$) is $I_{F2} = a_2\tau_2 > 79\%$ at 510 nm and $I_{F2} > 97\%$ at 560 nm (NP68). This component shows always positive pre-exponential values (see Table 2) and then it is assigned to the decay time of the relaxed AECPV3.

The longest component (τ_1) has a small contribution to the overall decay (<4%). This component arises from the presence of an impurity in the samples, which could be separated from the AECPV3 by preparative thin layer chromatography (TLC) with silica gel plates, and also by HPLC. However, the fluorescence decays of the "purified" AECPV3 samples still showed the presence of this longest temporal component, but in a smaller amount, indicating the difficulty for a complete removal of this component. The existence of vinylene bonds in *cis*-conformation was discarded after refluxing the samples in toluene with iodine, in order to promote the *cis* to *trans* isomerisation, and no changes were observed in the fluorescence decays measured later with the treated samples. In summary, the fluorescence decays of the AECPV3 are double-exponential. The two decay times and respective pre-exponential coefficients are not affected by the presence of the residual impurity because its decay time is sufficiently longer, therefore any mixing with the former decay times is negligible. However, fluorescence decays of NP68 measured with 0.814 ps/channel indicate the presence of a 8 ps component, which most probably represents the slow part of the solvation dynamics (see Supporting Information).

Fluorescence Decays (Excitation at 370 nm)

We have also analyzed the possibility of intramolecular energy and/or electron transfer upon direct excitation of the amine moiety of NP71. In Figure 4, normalized emission spectra of the end-capped NP71 obtained with excitations at 370 nm and 440 nm are shown. With excitation at 370 nm (absorption maximum of the styryl-phenyl amine), a residual emission can be seen in the spectral region where the emission of the individual amine is observed (ca. 400–470 nm; see also Figure 2). Excitation spectra (not shown) measured by setting the emission wavelength at 440 nm are in agreement with the absorption spectrum of the styryl-phenyl group, indicating that the differential emission shown in Figure 4 corresponds to the fluorescence of the amine.

Fluorescence decays of NP71 in methylcyclohexane (MCH) measured with excitation at 288 or 370 nm and emissions at 500 and 600 nm are identical to those obtained by exciting at 440 nm. The residual emission at 430 nm shows essentially the decay time of the styryl-phenyl amine (1.31 ns). Therefore, the emission at 400–470 nm is assigned to free amine that remains as impurity.

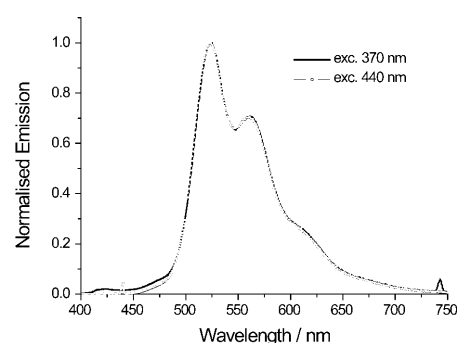


Figure 4. Normalized emission spectra of NP71 in MCH at 293 K, obtained with excitation at 370 nm and 440 nm. With excitation at the amine (370 nm) a residual emission is observed in the high energy spectral region.

Solvent and Temperature Effects

Fluorescence decays of the end-capped NP68 in different solvents, with viscosities from 0.6 cP (toluene) up to 2.3 cP (*n*-tetradecane) at 293 K, were measured with excitation at 440 nm at two emission wavelengths (500 and 600 nm). As with the corresponding trimer, the fast component value of the fluorescence decays increased when the solvent viscosity was raised (Table 3). The other components remained roughly constant.

The temperature effect on the fluorescence decays was also tested using NP68 in toluene. From 293 K to 333 K, the longest 1.44 ns and intermediate 0.79 ns components remained approximately constant as did the corresponding pre-exponential coefficients. The fastest decay component decreased from 47 ps at 293 K to 30 ps at 333 K, showing that this component is associated with an activated process, in agreement with the behavior observed for the trimers used in the synthesis of the

Table 3. Viscosity dependence of the fastest decay time (τ_3) of NP68, in solvents of different viscosity (η) at 293 K.

Solvent	η [cP]	τ_3 [ps]
Toluene	0.58	47
Decane	0.93	54
Dodecane	1.51	66
Tetradecane	2.34	87

AECPV3.^[11] Figure 5 shows the Arrhenius plot of the reciprocal decay time, from which an activation energy of 2.17 kcal mol⁻¹ is obtained. This value is very close to the activation energy of viscous flow of toluene ($E_{\eta} = 2.09$ kcal mol⁻¹) as found with the non-end-capped oligomer MBOPV3.^[11]

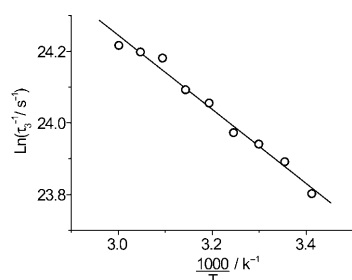


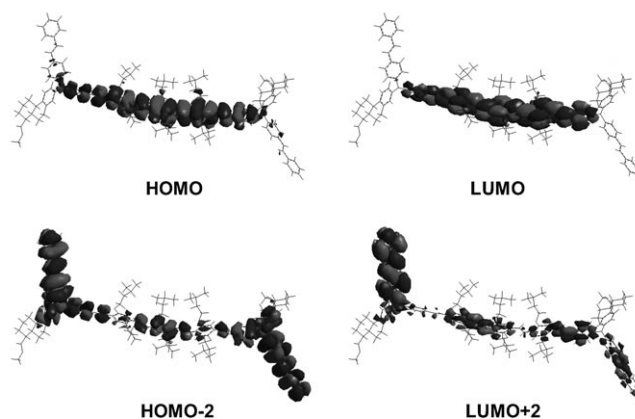
Figure 5. Arrhenius plot for the reciprocal fastest decay time τ_3 of NP68 in toluene (activation energy $E_a = 2.17$ kcal mol⁻¹).

Nature of the Excited States of the AECPV3s

The introduction of the amine groups in the PV-trimers red-shifts the absorption and emission maxima by ca. 30 nm and 40 nm, respectively, thus suggesting that the π -conjugation of the PV backbone is extended to the terminal groups. Molecular orbital calculations show that the lowest energy absorption band at 468 nm essentially results from a HOMO–LUMO transition ($\lambda_{\text{calc}} = 438$ nm; $f = 2.65$), in which the orbital delocalization is extended just to the two terminal phenyl groups belonging to the end-capped amines (Scheme 1).

The calculations predict two singlet–singlet transitions HOMO→LUMO+1 ($\lambda_{\text{calc}} = 364$ nm; $f = 0.09$) and HOMO–2→LUMO+2 ($\lambda_{\text{calc}} = 340$ nm; $f = 1.84$) in the wavelength region where the additional band at 379 nm, characteristic of the styryl–phenyl compounds (NP71 and NP73), is observed. On the basis of the oscillator strengths f we assign the 379 nm band to the quasi-locally-excited transition HOMO–2→LUMO+2 (Scheme 2), which is consistent with the relatively small red-shift of this band with respect to the free amine (370 nm). Thus, excitation of NP71 or NP73 at 370 nm should be followed by sub-picosecond internal conversion to S_1 . This is spatially equivalent to intramolecular energy transfer from the end-capped amine to the trimer backbone. Therefore, the long-lived (1.31 ns) residual emission at 430 nm (observed with excitation at 370 nm) can only be due to an impurity.

In summary, the incorporation of end-capped amines in the PV trimers does not substantially affect the properties of the first excited singlet state: There are red shifts of absorption and emission spectra that are compatible with the extended delocalization to the two terminal amine phenyl groups, and both the radiative, k_{r} and sum of the radiationless rate constants, k_{NR} , increase as expected from the increase of the transition dipole moment (oscillator strength) and number of vibrational modes, respectively. The increase of k_{NR} is larger than that of k_{r} which results in a lower fluorescence quantum yield of the end-capped trimers. In the case of the styryl–phenyl amine-end-capped trimers NP71 and NP73, there is a subpico-



Scheme 2. Calculated HOMOs and LUMOs for AECPV3s.

second-lived quasi-locally-excited state on the amine moiety, which may be relevant in electron-hole combination in EL devices.

The modest decrease on Φ_{f} from the trimers to the amine-end-capped derivatives was at first surprising because aromatic amines are well-known electron donors, even in nonpolar solvents. The absence of efficient intramolecular electron/charge transfer from the amine to the trimer moieties seems to result from substantial stabilization of the nitrogen lone pair in the derivatives. According to the MO calculations, the “lone pair” belongs to the HOMO-2, which is lower in energy than the HOMO.

Conformational Relaxation

The first absorption band of the AECPV3s is unstructured, while the emission spectra exhibit vibronic structure with relative intensities decreasing in the 0- n vibronic transition order (Figure 1). Given the weakly polar nature of solutes and solvent, the large Stokes shift suggests conformational differences between the ground- and the excited state,^[16] with more planar species in the relaxed excited state, absorbing and emitting at lower energy.

Table 2 shows that increasing the van der Waals volume of the AECPV3 end-groups and/or side chains, the shortest decay time τ_3 increases. The two longest decay times remain approximately constant. The same observation was made with the parent trimers MBOPV3 and EHOPV3, where the relaxation time was seen to increase from the smaller (methylbutyloxy) to the larger (ethylhexyloxy) side-chain.^[11] In Figure 6, the shortest decay time τ_3 of the AECPV3 (Table 2) is plotted against the sum of the van der Waals volumes of end-groups and side-chains (V_{w}). A linear fit is obtained with all compounds, including the two parent trimers. The increase of τ_3 is the expected result for a rearrangement of the AECPV3 backbone requiring significant displacement of both side and end-groups through the solvent.

The log–log plot of τ_3 vs V_{w} is also linear with a slope very close to 1 (0.95). This linear dependence of τ_3 on volume is reminiscent of the behavior expected from the Debye-Stokes-

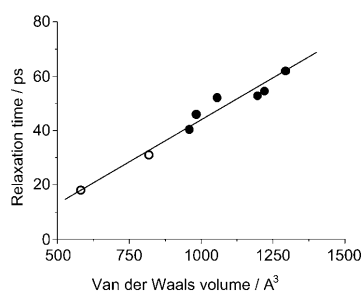


Figure 6. Plot of the shortest decay time τ_3 vs the sum of the van der Waals volumes of end-groups and side-chains for the AECPV3s (●) and MBOPV3 and EHOPV3 (○).

Einstein (DSE) equation^[17] for the rotational time of a sphere $\tau_{\text{rot}} = \eta V / k_B T$, which also predicts such relationship. This result (slope ≈ 1) is totally unexpected because the conformational (torsional) relaxation of the backbone involves different solvent frictions (the push and pull of side-chains to and from the solvent and the twist of the amine groups), none of them being a pure rotational friction. Also interesting and surprising is the slope value from Figure 6 ($3 \times 10^{16} \text{ m}^{-3} \text{ s}$) which is only five-fold smaller than the theoretical value predicted from the DSE equation ($\eta / k_B T = 1.4 \times 10^{17} \text{ m}^{-3} \text{ s}$) for toluene at 293 K.

The torsional times found with the parent trimers MBOPV3 and EHOPV3, are proportional to η^α with $\alpha < 1$ (0.83 and 0.66 for MBOPV3 and EHOPV3, respectively).^[11] The limited number of solvents here employed, as compared to those used with trimers, is not sufficient to evaluate the α values of the AECPV3s, but the data obtained with NP68 (log–log plot of τ_3 vs η from data in Table 3, and $Ea \approx E\eta$ from the Arrhenius plot in toluene) clearly indicate α values close to 1 for the AECPV3s.

In summary, the effects of viscosity, temperature and end-group-plus-side-chain volume on the shortest decay time of the AECPV3s assign this time to structural relaxation of the AECPV3 backbone, leading to more planar conformations. Moreover, the AECPV3s and parent trimers clearly reveal the effect of volume of side- and end-groups on the conformational relaxation.

Conclusions

The major conclusions of this work are: 1) incorporation of end-capped amines in the PV trimers does not substantially affect the properties of the first excited singlet state; 2) no evidence was found for intramolecular electron transfer from amine to trimer; 3) the AECPV3 compounds show conformational relaxation dependence on solvent viscosity and temperature as observed with the parent trimers; 4) the conformational relaxation times display a linear relationship with the van der Waals volume of end-group-plus-side-chain.

Experimental Section

Materials: Methylcyclohexane (MCH), analytical grade, was purchased from BDH. Toluene (Spectranal) was purchased from Riedel-

de Haën. The solvents were free of fluorescent impurities with excitation in the 370–450 nm range. The concentration in solution of the AECPV3 was $(1\text{--}2) \times 10^{-6} \text{ M}$. For this concentration the absorbance values at the maximum were ca. 0.10.

The synthesis of the phenylenevinylene trimers, 2,5-di-[(2-ethylhexyl)-oxyl]-*p*-phenylenevinylene (EHOPV3) and 2,5-di-[(3-methylbutyl)-oxyl]-*p*-phenylenevinylene (MBOPV3), was previously described.^[18] The general synthesis of the abietic acid based amine end-capped *p*-phenylenevinylene trimers (AECPV3; Scheme 1) was carried out as follows.

A solution of EHOPV3 or MBOPV3 (0.045 mmol) and 4-bromobenzyl triphenylphosphonium bromide (0.11 mmol) in a mixture of anhydrous methanol and tetrahydrofuran ($v/v = 50/50$, 4 mL) was placed in a schlenk tube under argon atmosphere. A 30 wt% sodium methoxide solution in methanol (0.23 mmol) was added dropwise and the reaction mixture was stirred at ambient temperature until complete consumption of the trimer (2–4 h) as monitored by TLC. The reaction mixture was diluted with diethylether, washed with a 3 N solution of hydrochloric acid and brine. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The product obtained was dried under vacuum and used without further purifications.

Terminal Di-(Bromophenyl)- 2,5-Di-[(3-Methylbutyl)-oxyl]-*p*-Phenylenevinylene Trimer (BPMBOPV3): With MBOPV3 (0.058 mmol, 50 mg) and 4-bromobenzyl triphenylphosphonium bromide (0.15 mmol, 74 mg) BPMBOPV3 was afforded as an orange amorphous solid (dichloromethane/diethyl ether, 64 mg, $\eta = 95\%$). IR (KBr): $\nu_{\text{max}} = 3055, 2950, 2866, 1676, 1597, 1508, 1424, 1206, 1057, 966, 853 \text{ cm}^{-1}$. ¹H NMR (CDCl_3): $\delta = 0.98\text{--}1.03$ (m, 36H, CH_3), 1.78 (q, 12H, $J = 6.6 \text{ Hz}$, CH_2), 1.95 (hept, 6H, $J = 6.3 \text{ Hz}$, CH), 3.91–3.97 (m, 12H, OCH_2), 7.04–7.50 ppm (m, 22H, aromatic and vinyl CH). MALDITOF-MS m/z 1160.3 (M^+).

Terminal Di-(Bromophenyl)- 2,5-Di-[(2-Ethylhexyl)-oxyl]-*p*-Phenylenevinylene Trimer (BPEHOPV3): With EHOPV3 (0.045 mmol, 50 mg) and 4-bromobenzyl triphenylphosphonium bromide (0.11 mmol, 58 mg) BPEHOPV3 was afforded as an orange amorphous solid (61 mg, $\eta = 96\%$). FTIR (KBr): $\nu_{\text{max}} = 3056, 2958, 2926, 2858, 1654, 1508, 1421, 1202, 1038, 725, 542 \text{ cm}^{-1}$. ¹H NMR (CDCl_3): $\delta = 0.87\text{--}1.03$ (m, 36H, CH_3), 1.25–1.68 (m, 48H, CH_2), 1.82 (hept, 6H, $J = 5.7 \text{ Hz}$, CH), 3.91–3.97 (m, 12H, OCH_2), 7.05–7.53 ppm (m, 22H, aromatic and vinyl CH). MALDITOF-MS m/z 1412.6 (M^+).

General Procedure for the Synthesis of AECPV3: To a mixture of diarylamine (0.038 mmol), BPMBOPV3 or BPEHOPV3 (0.018 mmol), sodium *tert*-butoxide (0.040 mmol) in dry *o*-xylene (0.4 mL) under an argon atmosphere in a Schlenk tube, tri-*tert*-butylphosphine (5.0 μL) and palladium acetate (1 mg) were added. The mixture was stirred at 120 °C until complete consumption of amine (4 h) as monitored by TLC. The reaction mixture was then cooled to room temperature, taken up in diethyl ether (5 mL) and washed with brine. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The product obtained was isomerized to all-*trans* configuration by dissolving it in dry toluene and refluxing the solution overnight with a catalytic amount of iodine. The reaction mixture was washed with a solution of sodium metabisulfite, and then the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue obtained was purified by silica column chromatography using toluene or mixtures of diethyl ether/petroleum ether (1.5:3.5 to 1:1) or dichloromethane/toluene (1:1) as eluent.

Full details of the syntheses and characterization of the amine end-capped phenylene vinylene trimers can be found in the Supporting Information.

UV/Vis Absorption and Fluorescence: Absorption and fluorescence spectra were measured in a Beckman DU-70 spectrophotometer and a SPEX Fluorolog 212I, respectively. The fluorescence spectra were collected with right angle geometry, in the S/R mode and corrected for optics, detector wavelength dependence (emission spectra) and lamp intensity wavelength dependence (excitation spectra). Fluorescence quantum yields were measured using α,ω -dicyano-pentathiophene as standard ($\Phi_F=0.42$ in benzene at 293 K),^[19] with excitation at 467 nm.

Fluorescence decays were measured using the picosecond time-correlated single-photon counting (TCSPC) technique. The pulsed (82 MHz) excitation source was a Ti: Sapphire laser Tsunami (Spectra Physics) pumped with a solid state laser Millennia Xs (Spectra Physics). The Tsunami output (720–900 nm) was frequency doubled (Model 3980 Spectra Physics), then depolarized, and finally vertically polarized. The sample emission passed through a second polarizer at the magic angle and a monochromator (H20 Jobin Yvon), and finally was detected with a microchannel plate photomultiplier (Hamamatsu, R3809u-50 MCP-PT) and a SPC-630 acquisition board (Becker and Hickl, GmbH). Alternate collection of 10^3 counts of pulse and sample were carried out until 10^4 counts at the maximum were reached. The experimental excitation pulse (FWHM = 19 ps) was measured using a LUDOX scattering solution in water, whose transmittance at the excitation wavelength was matched to that of the sample. The fluorescence signals were deconvoluted from the excitation pulse, using the LINUX version of George Striker's program.^[20] The time resolution of the apparatus is ca. 3 ps.^[21]

Molecular Orbital Calculations: Molecular orbital calculations were carried out using HyperChem 5.0 program.^[22] Molecular geometries were optimized using PM3 and single point calculations were performed using PM3-CI, AM1-CI and ZINDO/S-CI. The three methods gave results in qualitative agreement concerning the states order, oscillator strengths and molecular orbitals involved in the states.

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