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Singlet and triplet excitations of chiral dialkoxy-*p*-phenylene vinylene oligomers

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The excited state properties of a series of α,ω -dimethyl-oligo{2,5-bis[2-(*S*)-methylbutoxy]-*p*-phenylene vinylene}s (OPVns, with n the number phenyl rings) are investigated for $n=2-7$ in solution at ambient temperature, under matrix-isolated conditions at low temperature, and as nanoaggregates using absorption (time-resolved), photoluminescence, photoinduced absorption, circular dichroism, and circular polarized luminescence spectroscopies. The singlet ($S_1 \leftarrow S_0$) and triplet ($T_n \leftarrow T_1$) transition energies decrease with conjugation length. For the S_1 state of OPVn the lifetime strongly decreases with chain length due to enhanced nonradiative decay and radiative decay. The increase in the nonradiative decay rate constant is much more pronounced, and as a result the photoluminescence quantum yield is less for longer oligomers. Studies at low temperature afforded spectra with well-resolved vibronic fine structure. Under these conditions the Stokes' shift is very small (≤ 0.04 eV). The Huang-Rhys parameter and relaxation energies in the excited state associated with $S_1 \leftarrow S_0$ and $T_n \leftarrow T_1$ transitions and their evolution with conjugation length have been determined via a Franck-Condon analysis of the vibronic fine structure. For OPV7, the relaxation energy of S_1 with respect to S_0 (0.165 ± 0.02 eV) is considerably larger than for T_n with respect to T_1 (0.03 eV), but the latter increases for the shorter oligomers, in contrast to the relaxation energy of S_1 . The OPVns ($n \geq 5$) form nanoaggregates in polar solvents such as ethanol. The changes in absorption and emission together with a strong circular dichroism and circularly polarized emission indicate the formation of chiral H-type aggregates under these conditions.

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I. INTRODUCTION

Conjugated polymers attract considerable attention for their use in polymer light-emitting diodes, as an active component of optically pumped lasers, in photovoltaic devices, and in all-plastic electronics.¹ These materials combine some of the attractive functional properties of traditional semiconductors with solubility in common organic solvents and, hence, easy processability. π -conjugated polymers usually have a strongly dipole-allowed electronic transition in the visible region of the spectrum and certain types [e.g., poly(*p*-phenylene vinylenes) or PPVs] show efficient luminescence in solution and thin solid films. In the past decade, the nature of the excited state(s) involved in these spectroscopic transitions has been intensely debated.² Well-defined oligomers serve an important role in studying the mechanisms involved in photoexcitation of conjugated polymers and in determining the nature and the decay of their excited states. The main advantage of investigating the nature and temporal evolution of photoexcitations of conjugated oligomers is their well-defined molecular structure, which allows structure-property relations to be determined in great detail and to evaluate the effect of increasing conjugation length and estimate properties for the more complex polymer.³

Although oligo(*p*-phenylene vinylene)s (OPVns, $n=2$

to 8, with n the number of phenyl rings) were first synthesized by Drefahl and Plötner as early as 1961,^{4,5} the number of reports on optical and electronic properties of OPVns is limited.³ The most intensively studied set of OPVns is a homologous series ($n=2-7$) with *tert*-butyl groups in the 3,5-positions of the terminal phenyl rings to provide increased solubility, prepared by Müllen *et al.*⁶ The fluorescence,⁷⁻⁹ vibrational spectra,^{10,11} photoconductivity¹² and triplet state absorption¹³ of these materials have been studied. More recently, the synthesis and optical properties in solution of a series of oligo(2,5-dipropoxy-*p*-phenylene vinylene)s ($n=2-12$) has been described by Meier *et al.*^{14,15} Recently these oligomers have been incorporated as the active material in light-emitting diodes.¹⁶

Here we present the detailed characterization of the optical properties in the ground state and singlet and triplet excited state of a series of novel chiral methyl end-capped 2,5-bis(2-(*S*)-methylbutoxy)-1,4-phenylene vinylene oligomers with 2 to 7 phenyl rings.¹⁷

These OPVns have been investigated in solution at ambient temperature, under matrix-isolated conditions at low temperature, and as nanoaggregates. The evolution of the absorption, emission, radiative and nonradiative decay constants, and triplet state absorption and lifetime with increasing conjugation is determined. It will be shown that at low temperature the inhomogeneous broadening is significantly reduced as a result of conformational relaxation to a more

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uniform molecular geometry, providing well-resolved spectra for which a Franck–Condon analysis affords an estimate of the relaxation energy in the singlet and triplet excited states. For the nanoaggregates, study of absorption and fluorescence together with circular polarization in absorption and luminescence provides evidence that the optical properties resemble those of H-aggregates.

II. EXPERIMENT

The preparation of the OPVns has been reported elsewhere.¹⁷ Optical spectra were recorded using a Perkin Elmer Lambda 900 spectrophotometer for UV/Vis absorption, a Jasco J-600 spectropolarimeter for circular dichroism, a Perkin Elmer LS50B and a SPEX spectrometer for fluorescence. For fluorescence spectra a 2 nm bandwidth was used and the optical density of the solutions was 0.1 at the excitation wavelength (0.05 for quantum yield determinations). The fluorescence spectra have been corrected for the wavelength dependence of the sensitivity of the detection system. Photoluminescence quantum yields were determined against quinine bisulfate in 1 N aqueous H₂SO₄ ($\phi_{\text{PL}}=0.546$) and fluorescein sodium salt in 0.1 N aqueous NaOH ($\phi_{\text{PL}}=0.93$) and corrected for differences in refractive index.^{18,19} A homebuilt 16-channel PMT based instrument was used for circularly polarized luminescence, in which the emission detector is in a direction perpendicular to the excitation beam. To avoid artifacts due to photoselection, the excitation light was linearly polarized in the plane spanned by excitation and emission beams. For fluorescence lifetime measurements a ~ 5 ps exciting light pulse at 300 nm was obtained by frequency doubling the output of a synchronously pumped cavity dumped dye laser which was operated at a repetition rate of 0.48 MHz. The dye laser (operated at 600 nm) was pumped with the frequency-doubled output of an actively stabilized mode-locked Nd:YAG laser. The fluorescence light, collected in a backward-scattering geometry, was dispersed by a 0.34 m double monochromator allowing for a spectral resolution of 1 nm. Fluorescence decay curves were recorded with the time-correlated single photon counting technique in reversed mode using a microchannel plate photomultiplier (Hamamatsu R3809u-51). Instrument response function is ~ 60 ps FWHM. Photoinduced absorption (PIA) spectra were recorded between 0.25 and 3.5 eV by exciting with a mechanically modulated cw Ar-ion laser (458 nm) pump beam and monitoring the resulting change in transmission (ΔT) of a tungsten-halogen probe light through the sample after dispersion by a triple grating monochromator and detection, using Si, InGaAs, and cooled InSb detectors.

PIA spectra were recorded with the pump beam in an almost parallel direction to the probe beam. To avoid interference of the very strong photoluminescence of the OPVns in the PIA spectra we used a double modulation technique which allowed for the direct discrimination between photoinduced absorption and photoluminescence. The key feature of this technique is to modulate the excitation light (pump beam) at low frequency (75 Hz) and the probe light at higher frequency (3.5 kHz). The resulting detector signal was first amplified by a phase sensitive lock-in amplifier referenced to the frequency of the probe beam. The in-phase output of the first lock-in amplifier, corresponding to the transmission (T), was then used as the input to a second phase sensitive lock-in amplifier referenced to the pump beam frequency. Since only the photoinduced absorption and bleaching signals carry the high and low frequency modulation, the second lock-in amplifier gives ΔT without contamination from a photoluminescence signal and the photoinduced absorption, $-\Delta T/T \approx \Delta\alpha d$, is directly calculated from the outputs of the lock-in amplifiers. The pump power incident on the sample was typically 50 mW with a beam diameter of 2 mm. For the determination of the lifetime a single modulation technique was used and data were corrected for the photoluminescence contribution by subtraction. Low temperature spectra were recorded using an Oxford Optistat continuous flow cryostat; during measurements the temperature was kept constant within 0.1 K. Spectra at different temperatures are not corrected for volume changes of the solvent. In order to prepare OPVn nanoaggregates in poor solvents a few drops of a concentrated OPVn solution in chloroform (good solvent) were mixed at room temperature with the poor solvent.

III. RESULTS AND DISCUSSION

A. Optical spectra of OPVns in solution

The UV/Vis absorption and photoluminescence spectra of the OPVns recorded at room temperature in 2-methyltetrahydrofuran (2MeTHF) solution are shown in Fig. 1 and Fig. 2. In chloroform identical absorption spectra were recorded, while the emission shifts slightly to longer wavelengths by 7–10 nm (Table I). Analogous to the results described by Meier *et al.*,²⁰ the optical transitions of the

FIG. 1. UV/Vis absorption spectra of OPVns recorded in 2MeTHF at 290 K. The spectra were normalized to unit intensity.

FIG. 2. Photoluminescence spectra of OPVns recorded in 2MeTHF at 290 K. The spectra were normalized to unit intensity.

OPVns shift to longer wavelengths with increasing conjugation length. The decrease of the transition energies (Table I, Fig. 3) is almost linear with $1/n$, but for the longest oligomers a deviation from a linear relation is observed, pointing at a possible convergence limit. To account for a convergence limit of the conjugation length in π -conjugated oligomers, Meier *et al.* have proposed a model to describe the energies of the optical transitions as a function of the conjugation length.²⁰ According to this model the transition energy of an oligomer, $E(n)$, with n repeating units is described by the equation:

$$E(n) = E_{\infty} + [E(1) - E_{\infty}] \exp[-a(n-1)], \quad (1)$$

in which $E(1)$ represents the transition energy of the monomer ($n=1$) and E_{∞} the limiting value of $E(n)$ for $n \rightarrow \infty$. The difference $E(1) - E_{\infty}$ characterizes the overall effect of conjugation and the parameter a is an indication of how fast the convergence limit is reached. When the experimental data are fitted to this equation, the agreement is excellent and the fitting parameters (Table II) are in full agreement with those reported by Meier for related OPVns.²

The molar absorption coefficients (ϵ) of the π - π^* absorption bands increase linearly with the number of phenyl rings (Table I). The transition dipole moments (μ), determined by spectral integrating over the π - π^* absorption band

FIG. 3. Chain length dependence of the optical transitions. Lines represent fits according to the model described in Eq. (1).

(Table I), increase with chain length, similar to the molar absorption coefficient, albeit, in a sub-linear fashion. There is no indication that μ starts to converge for OPV7 (16.1 D), in full agreement with recent INDO/SCI calculations which place the transition dipole moments of OPV5 and OPV11 at 17.3 and 26.5 D, respectively.²¹ The highest quantum yields for fluorescence (ϕ_{PL}) are found for OPV3 (62%) and OPV4 (76%). A significant decrease of ϕ_{PL} occurs for the longer oligomers. The lifetime of the singlet excited state (τ) has been determined using single photon counting time-resolved photoluminescence in toluene at room temperature by exciting at 300 nm (Fig. 4). The decay curves, shown in Fig. 4, have been fitted to a single exponential decay. The resulting time constants (Table I) reveal that there is a considerable reduction of the excited state lifetime with increasing conjugation length from 1.70 ns for OPV3 to 0.45 ns for OPV7. Studies on OPV7 in a variety of organic solvents revealed that τ is independent on the nature of the medium. The sin-

TABLE I. Room-temperature optical data of OPVns.

OPVn	CHCl ₃		2MeTHF		ϵ^a (1/mol/cm)	ϕ_{PL}^a	τ^b (ns)	k_r^c $\times 10^8$ (s ⁻¹)	k_{nr}^c $\times 10^8$ (s ⁻¹)	μ^d (D)
	$S_1 \leftarrow S_0$ (eV)	$S_1 \rightarrow S_0$ (eV)	$S_1 \leftarrow S_0$ (eV)	$S_1 \rightarrow S_0$ (eV)						
OPV2	3.47	3.03	3.46	3.10	21 000	-	-	-	-	4.8
OPV3	3.05	2.66	3.05	2.71	44 000	0.62	1.70	3.7 $\pm$ 1	2.2 $\pm$ 1	7.8
OPV4	2.84	2.47	2.84	2.51	68 000	0.76	1.32	5.8 $\pm$ 1	1.8 $\pm$ 1	10.0
OPV5	2.73	2.37	2.73	2.41	88 000	0.49	0.73	6.7 $\pm$ 1	7.0 $\pm$ 1	12.1
OPV6	2.67	2.32	2.66	2.37	107 000	0.41	0.52	8.0 $\pm$ 2	11.3 $\pm$ 2	13.1
OPV7	2.61	2.29	2.62	2.32	142 000	0.25	0.45	5.5 $\pm$ 2	16.7 $\pm$ 2	16.1

^aMolar absorption coefficient (ϵ) and photoluminescence quantum yield (ϕ_{PL}) in CHCl₃.

^bSinglet state life time in toluene.

^cRadiative (k_r) and nonradiative (k_{nr}) decay constants.

^dTransition dipole moment in 2MeTHF.

TABLE II. Conjugation analysis of optical transitions of OPVns.^a

<i>T</i> (K)	Transition	Vibronic	<i>E</i> _∞ (eV)	<i>E</i> (1)− <i>E</i> _∞ (eV)	<i>a</i>
290	<i>S</i> ₁ ← <i>S</i> ₀	at λ _{max}	2.58	1.63	0.62
290	<i>S</i> ₁ ← <i>S</i> ₀	(0-0)	2.30	1.56	0.68
80	<i>S</i> ₁ ← <i>S</i> ₀	(0-0)	2.28	1.72	0.59
80	<i>S</i> ₁ ← <i>S</i> ₀	(0-0)	2.24	1.73	0.59
100	<i>T</i> _n ← <i>T</i> ₁	(0-0)	1.37	1.40	0.40

^a*E*_∞*E*(1) and *a* are defined in Eq. (1).

glet excited state lifetime for OPV7 ($\tau=0.45$ ns) is slightly higher than for poly(2-methoxy5-(2'-ethylhexoxy)-1,4-phenylene vinylene) (MEH-PPV) in solution ($\tau=0.33$ ns).²² For MEH-PPV, the reported quantum yield for fluorescence ($\phi_{\text{PL}}=0.35$), is somewhat larger than the value obtained for OPV7 (Table I).

Using the values for τ and ϕ_{PL} it is possible to estimate radiative (k_r) and nonradiative (k_{nr}) rate constants using:

$$\phi_{\text{PL}} = \frac{k_r}{k_r + k_{\text{nr}}} \quad (2)$$

and

$$\frac{1}{\tau} = k_r + k_{\text{nr}}. \quad (3)$$

The values for k_r and k_{nr} (Table I) reveal that k_r increases with conjugation length. The increase of k_r with conjugation length is consistent with the Strickler–Berg expression for the fluorescence lifetime of molecules.¹⁹ The increase in the molar absorption coefficient (ϵ) outweighs the decrease in the cube of the transition energy ($h\nu$) with increasing n , and hence, k_r is predicted to increase from OPV3 to OPV7 by a factor of about 2 based on the Strickler–Berg relation, in qualitative agreement with the experimental values (Table I). The major change in the decay is due to the nonradiative decay constant k_{nr} which increases by a factor of ~ 7 – 8 going from $n=3$ to 7 . This behavior is opposite to the trend observed for oligothiophenes (nT) for which k_{nr} decreases for $n=2$ – 5 and then reaches a constant value for

FIG. 4. Time-resolved photoluminescence of OPVns in toluene recorded at 300 K by exciting at 300 nm and monitoring the emission at 500 nm ($n=3$) and 530 nm ($n=4, 5, 6$, and 7). The maximum emission was normalized to 1000 counts.

FIG. 5. Temperature dependence of the UV/Vis absorption of OPV5 dissolved in 2MeTHF recorded in the range from 290 K to 80 K, by cooling in 10 K steps. The assignment of the vibronic bands (0- n) of the $S_1 \leftarrow S_0 \pi-\pi^*$ absorption is indicated. The inset shows the vertically expanded spectrum recorded at 80 K to show presence of the higher energy $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions more clearly.

$n=5$ – 7 .²³ The increase of k_{nr} may be explained by an increase of the rate for intersystem crossing to the triplet state or by an increase in the rate for internal conversion.²⁴ Reduction of the quantum yield for fluorescence by aggregate formation, as observed for dye molecules, seems unlikely at these low concentrations in chloroform and would mainly lead to a decrease in the radiative decay rates, which does not appear to be the case (Table I).

B. Optical spectra of OPVns in a glassy matrix

The change of the UV/Vis spectra of the OPVns with temperature is significant. In Fig. 5 the UV/Vis spectra of OPV5 in 2MeTHF recorded in the temperature range 290–80 K are shown as an example. At 290 K the UV/Vis absorption spectrum consists of an inhomogeneously broadened $\pi-\pi^*$ absorption band with $\lambda_{\text{max}}=445$ nm. With decreasing temperature the absorption maximum shifts gradually to higher wavelengths and around 150 K vibronic fine structure appears in the spectrum. Cooling below 150 K causes a significant narrowing of the vibronic features and at 80 K three to four vibronic bands can be distinguished. At 80 K the 0-0 transition ($\lambda_{\text{max}}=507$ nm) has gained the highest intensity. Subsequent cooling from 80 to 10 K (not shown) does not result in a further change of the spectrum. These changes with temperature are interpreted as a continuous loss of conformational freedom resulting in a planarization of the geometry of OPV5 and a more uniform molecular structure. In agreement with this model the onset of the $\pi-\pi^*$ band shifts only slightly with temperature, but the absorbance at 507 nm increases with more than one order of magnitude. The changes with temperature come to a stop at 80 K where the 2MeTHF matrix completely rigidifies. Similar well-resolved spectra have been obtained for the other OPVns (Fig. 6). The spacing between the vibronic bands in the absorption spectra ranges from 1300 to 1450 cm^{-1} , consistent with a C=C stretch vibration mode. A plot of the energies of 0-0 vibronic transitions of the $S_1 \leftarrow S_0$ band for the OPVns

FIG. 6. UV/Vis absorption and photoluminescence spectra of OPVns recorded in 2MeTHF at 80 K. The spectra were normalized to unit intensity.

versus the reciprocal number of phenyl rings in the oligomers is shown in Fig. 3. As can be seen from Fig. 3, Eq. (1) also fits the low temperature $S_1 \leftarrow S_0$ absorption data of oligomers. The values for E_∞ , $E(1) - E_\infty$, and a are collected in Table II and reveal that at 80 K the overall conjugation has increased and that the convergence limit will be reached for longer oligomers. In addition to the vibronically resolved $S_1 \leftarrow S_0$ transition, the low temperature UV/Vis spectra also show a number of less intense transitions at higher energies (Fig. 5). The bands are tentatively assigned to transitions involving the second ($S_2 \leftarrow S_0$) and third ($S_3 \leftarrow S_0$) excited singlet states. Similar to $S_1 \leftarrow S_0$, the energy of these higher transitions also decreases with chain length (Fig. 3).

The change in temperature also has a strong effect on the photoluminescence of the OPVns (Fig. 6). The photoluminescence spectra recorded in 2MeTHF at 80 K exhibit a well-resolved vibronic progression with a spacing between the 0-0 and 0-1 transitions of $1350\text{--}1450\text{ cm}^{-1}$. The excitation spectra of the low temperature fluorescence of the

OPVns closely resemble to the corresponding absorption spectra and also reproduce the bands to the S_2 and S_3 excited states. Under these low temperature conditions in 2MeTHF, the Stokes' shift is very small, varying between 0.02 and 0.04 eV (Table III).

The relative intensity of the $S_1 \rightarrow S_0$ 0-0 electronic transition in the photoluminescence increases with increasing conjugation length. The intensity of the consecutive vibronic bands in the absorption and emission spectra is governed by the Franck-Condon factors. In the harmonic approximation, the intensities of the transitions between the vibrational ground state 0 in the electronic excited state and the vibronic level n in the ground state are given by:

$$I_n = \frac{e^{-S} S^n}{n!}, \quad (4)$$

where S is the Huang-Rhys factor that describes the extent of the geometry deformation in the excited state (S is proportional to the square of the displacement). In Fig. 7 the relative intensities of the first four vibronic transitions in the absorption and emission spectra of the OPVns in glassy 2MeTHF at 80 K are plotted. Figure 7(a) shows that in the absorption spectra the relative intensities are very similar for all OPVns and can accurately be described with a Huang-Rhys parameter $S = 0.95 \pm 0.05$. Knowledge of the Huang-Rhys factor allows to determine the amplitude of the relaxation energy (E_{rel}) in the excited state by multiplying with energy of the associated vibrational mode: $E_{\text{rel}} = S \cdot 1400\text{ cm}^{-1} = 1330 \pm 100\text{ cm}^{-1}$ ($0.165 \pm 0.02\text{ eV}$), which is in excellent agreement with the values of small oligo(*p*-phenylene vinylene)s obtained by Beljonne *et al.* based on theoretical calculations.²⁴ It must be noted, however, that these calculations predict a decrease of the relaxation energy with increasing chain length. The experimental absorption spectra, summarized in Fig. 7(a), do not show this expected effect very clearly. At this point it must be noted that the Stokes' shift of $\sim 0.03\text{ eV}$ is not related to the intrinsic relaxation energy (E_{rel}) of the OPVn molecules in the excited state, but rather reflects the reorganization energy inflicted by the surrounding solvent molecules in response to formation of the singlet excited state. Hence, the Stokes' shift can be considerably less than E_{rel} , as found in the present case for OPVns in a glassy 2MeTHF matrix.

TABLE III. Low temperature optical data of OPVn.

OPVn	$S_1 \leftarrow S_0$ (eV)	$S_2 \leftarrow S_0$ (eV)	$S_3 \leftarrow S_0$ (eV)	$S_1 \rightarrow S_0$ (eV)	Stokes' shift (eV)	$T_n \leftarrow T_1$ 0-0 (eV)	$T_n \leftarrow T_1$ 0-1 (eV)	α^a	τ^b (ms)	S^c
OPV2	3.24	4.11	4.90	3.21	0.033					
OPV3	2.81	3.85	-	2.79	0.025	2.00	2.27	1.03	7.9	-
OPV4	2.57	3.56	4.13	2.54	0.032	1.80	-	1.01	3.6	0.60
OPV5	2.45	3.46	3.87	2.41	0.038	1.65	1.80	0.96	3.4	0.37
OPV6	2.38	3.22	3.76	2.34	0.031	1.56	1.72	1.01	3.7	0.26
OPV7	2.33	3.09	3.66	2.30	0.026	1.50	1.65	0.98	2.9	0.20

^a α is the power-law exponent of the excitation intensity dependence of the PIA signal defined by $-\Delta T \propto I^\alpha$.

^bTriplet state lifetime.

^cHuang-Rhys parameter for $T_n \leftarrow T_1$ absorption.

FIG. 7. Relative intensities of the different vibronic transitions in absorption $S_1 \leftarrow S_0$ (a) and emission $S_1 \rightarrow S_0$ (b) of the OPVns dissolved in 2MeTHF at 80 K. The legend in (a) identifies the symbols for the different OPVns; the legend in (b) gives the S parameters for the emission for the same OPVns.

The Huang–Rhys parameters can also be determined from the emission spectra [Fig. 7(b)]. In comparison with the absorption data, the values of S determined from the emission spectra decrease more strongly with chain length and reach values less than 0.80 for the two longest oligomers. The reason for the differences between the Huang–Rhys factors in absorption and emission is likely associated with some residual conformational disorder present in the matrix at low temperature. Figure 5 indicates the possibility that not all molecules have relaxed to the lowest energy conformation at 80 K, causing a residual broadening of the absorption spectrum. In the excited state, the molecules tend to planarize further and the disorder is reduced. Hence the photoluminescence spectra are more representative of the properties of the lowest excited state, and suggest that the Huang–Rhys factor decreases with chain length.⁸

The validity of the approach to model the optical spectra with the use of Eq. (4) is shown in Fig. 8 where the experimental absorption and fluorescence spectra of OPV7 in 2MeTHF at 80 K (solid line) and corresponding spectral simulation are plotted. To model the absorption and photoluminescence spectra we used the Franck–Condon progression of Lorentzians and parameterized their height and width according to:

$$I(E) = \sum_{n=0} \frac{\Gamma^2}{(E - E_{00} \pm nE_n)^2 + \Gamma^2} \times \frac{I_n}{I_0}, \quad (5)$$

where Γ is the line width broadening parameter, E_n the vibronic spacing, E_{00} the 0-0 transition energy, I_n and I_0 are defined by Eq. (4), and + or – refer to emission and absorption respectively. The spectra shown in Fig. 8 were simulated using Eq. (5) and parameters $E_{00}=2.335$ eV, $E_n=0.165$ eV, $S=0.85$, and $\Gamma=0.052$ eV for absorption; and

FIG. 8. Experimental absorption and fluorescence spectra of OPV7 in 2MeTHF at 80 K (solid line) and corresponding spectral simulation (dashed line) using Eqs. (4) and (5) and parameters $E_{00}=2.335$ eV, $E_n=0.165$ eV, $S=0.85$, and $\Gamma=0.052$ eV for absorption; and parameters $E_{00}=2.300$ eV, $E_n=0.172$ eV, $S=0.73$, and $\Gamma=0.035$ eV for the emission spectrum.

parameters $E_{00}=2.300$ eV, $E_n=0.172$ eV, $S=0.73$, and $\Gamma=0.035$ eV for the emission spectrum. It must be noted that in this model we use only a single vibrational mode although it is known that more Raman-active modes appear in the 1000–1800 cm^{-1} range.¹⁰ Although the increasing width of the 0- n vibronic transitions in the experimental spectra indicate that additional modes contribute to the width of spectra, the experimental resolution does not allow for a more detailed analysis. As can be seen from Fig. 8 the agreement between experimental and simulated spectra is fair, although a significant deviation occurs at the onset of both the absorption and emission spectra.

C. Excited state absorption of OPVns in a glassy matrix

The excited state absorption of the OPVns dissolved in a 2MeTHF glass at 100 K in the microsecond to millisecond time domain was probed with a double modulation photoinduced absorption (PIA) spectrometer by exciting at 458 nm. The PIA spectra for OPV3–OPV7 recorded in this way are shown in Fig. 9. The photoinduced absorption in the OPVns is attributed to originate from the T_1 triplet excited state, and hence involves a $T_n \leftarrow T_1$ transition. This assignment is supported by the fact that the $T_n \leftarrow T_1$ photoinduced absorption bands increase linearly with the pump intensity ($-\Delta T \propto I^\alpha$, $\alpha \approx 1$; see Table III) as expected for a monomolecular decay mechanism. Furthermore the characteristic bands of charged photoexcitations (polarons), typically observed at energies below 1 eV are completely absent. The $T_n \leftarrow T_1$ transition energy decreases with increasing chain length (Fig. 3 and Fig. 9) in full agreement with previous results on related oligo(*p*-phenylene vinylene)s and theoretical calculations.^{13,24} The evolution of $T_n \leftarrow T_1$ transition energy with chain length when fitted to Eq. (1) reveals that $a=0.40$ (Table II) indicating that the convergence of the optical transition in the triplet state is reached at a later stage than for singlet transitions. The PIA spectra of OPV6 and OPV7 consist of strong 0-0 transitions, with one or two vi-

FIG. 9. PIA spectra of OPV n s recorded in 2MeTHF at 100 K using double modulation technique. Excitation was performed at 458 nm with 50 mW. The photoinduced absorption was normalized to 10^{-2} for each oligomer to allow for direct comparison. The dashed line in the PIA spectrum of OPV7 is a simulation using Eqs. (4) and (5) and parameters $E_{00}=1.505$ eV, $E_n=0.160$ eV, $S=0.20$, and $\Gamma=0.03$ eV.

brational shoulders at higher energy, spaced by ~ 0.16 eV. With decreasing chain length, the higher vibronic bands in the PIA spectra gain in relative intensity and as result the spectra broaden significantly. For OPV3, the 0-0 transition is less intense than the bands at higher energy. By varying the modulation frequency of the pump beam, it is possible to determine the lifetime of the T_1 excited state. A plot of the normalized photoinduced transmission (after correction for the photoluminescence) versus the modulation frequency is shown in Fig. 10 for OPV7. The experimental data can be fitted to the theoretical equation for the frequency dependence of $-\Delta T$ for a photoexcitation which decays in mono-molecular process:²⁵

$$-\Delta T \propto \frac{Ig\tau}{\sqrt{1+\omega^2\tau^2}}, \quad (6)$$

in which τ is the lifetime, ω the modulation frequency, I the intensity, and g the generation efficiency. The correspondence of Eq. (6) to the experimental data is good (Fig. 10) and gives $\tau=2.9$ ms for the lifetime of the triplet excited state in OPV7. The OPV n s measured in this way all have a similar lifetime, on the order of 3–4 ms (Table III), except for OPV3 for which $\tau=7.9$ ms under these conditions.

The result that the $T_n \leftarrow T_1$ absorption spectra of the longer OPV n s exhibit a single line is in full agreement with the theoretical result that the calculated oscillator strength originating from the T_1 state is concentrated in a unique T_n state, which is composed of singly excited configurations (LUMO $\leftarrow$ HOMO-1 and LUMO+1 $\leftarrow$ HOMO) and the doubly excited configurations (involving HOMO-1, HOMO,

FIG. 10. Intensity dependence of the PIA band at 1.50 eV of OPV7 in 2MeTHF as a function of the modulation frequency of the excitation beam. Data were recorded at 100 K by exciting at 458 nm and are corrected for photoluminescence. Solid line represents the fit for the expression for mono-molecular decay ($\tau=2.9$ ms). The inset shows the pump intensity dependence of $-\Delta T$, the solid line is a fit of $-\Delta T$ to a power law.

LUMO, and LUMO+1).²⁴ These calculations have also shown that the dispersion of the $T_n \leftarrow T_1$ absorption band with conjugation length results from a rather localized T_1 state in combination with a delocalized T_n state.

As noticed above, the PIA spectra for the longer oligomers exhibit almost a single line. For OPV7 we modeled the PIA spectrum (see inset of Fig. 9) using Eqs. (4) and (5) and parameters $E_{00}=1.505$ eV, $E_n=0.160$ eV, $S=0.20$, and $\Gamma=0.03$ eV. While the correspondence in the high energy tail is not very good, probably due to several contributing vibrational modes instead of one, the Huang–Rhys parameter in the triplet $T_n \leftarrow T_1$ absorption is clearly much lower than in the $S_1 \leftarrow S_0$ absorption and $S_1 \rightarrow S_0$ emission. The Huang–Rhys parameter in the $T_n \leftarrow T_1$ absorption increases significantly with decreasing chain length (Table III), from $S=0.20$ for OPV7 to $S=0.60$ for OPV4. As a consequence the relaxation energy in the T_n state increases from 0.03 eV to 0.09 eV in the same range.

D. Optical spectra of OPV n s in nanoaggregates

In polar solvents, such as primary and secondary alcohols, OPV7 forms nanoaggregates as a result of poor solubility.¹⁷ Figure 11 shows a transmission electron microscopy picture of the rodlike aggregates that can be formed in decanol. The extent of association and the size of the aggregates generally varies with sample preparation. For OPV7 the most reproducible results were obtained in ethanol. Typical UV/Vis and fluorescence spectra of OPV7 in ethanol are shown in Fig. 12. The OPV7 nanoaggregates show a significant hypsochromic shift of the absorption maximum ($\lambda=416$ nm, 2.98 eV) in comparison with the spectrum of OPV7 in chloroform ($\lambda=475$ nm, 2.61 eV). At the same time, the onset of the spectrum has shifted bathochromically from $\lambda \sim 550$ to ~ 575 nm. The fluorescence intensity of OPV7 nanoaggregates is quenched by at least one order of magnitude in comparison with the emission from free molecules in good solvents and the spectrum has shifted to lower

FIG. 11. Transmission electron microscopy of aggregates of OPV7. Samples were prepared on carbon-covered copper grids by putting a drop of an aggregated solution on the grid and subsequently removing the solvent after 10 s. The samples were stained with a thin layer of platinum. The length of the rodlike aggregates was determined to be several micrometers while the width of the aggregates vary between 20 and 200 nm. The white bar corresponds to 0.5 μm .

energy showing a first vibronic peak at $\lambda = 583 \text{ nm}$ (2.13 eV). A more accurate determination of the fluorescence quantum yield of the nanoaggregates was not successful, because of the varying extent of aggregation present in similarly prepared samples. The substantial decrease in fluorescence efficiency, however, is in accordance with previous results on nanoaggregates of oligothiophenes and (shorter) oligo(*p*-phenylene vinylenes).^{15,26} The emission at $\lambda < 550 \text{ nm}$ in Fig. 12 is attributed to OPV7 molecules that

FIG. 12. Optical spectra of OPV7 nanoaggregates in ethanol. Top: Normalized UV/Vis absorption and photoluminescence spectrum. Bottom: Wavelength dependence of the chiral anisotropy factors g_{abs} and g_{lum} as derived from the CD and CPL spectra of OPV7.

TABLE IV. Absorption and emission data of nanoaggregates of OPVns in ethanol.

	$S_1 \leftarrow S_0$ (eV)	$S_1 \rightarrow S_0$ (eV)	g_{abs}
OPV5	3.00	-	-0.9×10^{-3}
OPV6	3.03	2.19	-2.0×10^{-3}
OPV7	2.97	2.13	-2.4×10^{-2}

have not aggregated. We were able to prepare similar nanoaggregates for OPV6 and OPV5, but for $n < 5$ no such aggregates could be made in polar solvents. Surprisingly the absorption spectra differ only slightly for the different conjugation lengths (Table IV). The blue shift of the absorption maximum, the red shift of the onset of the absorption, and the loss of fluorescence intensity are characteristic of H-aggregates of OPVns, in which the molecules align with their transition dipole moments in a (nearly) parallel fashion.

A special property of the present OPVns is the fact that they carry chiral side chains and are optically active. As a consequence, the nanoaggregates exhibit circular dichroism (CD). The CD spectrum of OPV7 in ethanol exhibits a positive band at 397 nm and a negative band at 448 nm (Fig. 12). Such bisignate CD results from oscillator coupling between adjacent OPV7 chains in the nanoaggregate when there is a small angle between the transition dipole moments.²⁷ The interchain origin of the CD is consistent with the fact that no CD is observed when the OPVns are molecularly dissolved in chloroform. The chiral anisotropy factor, or g value of absorption, reaches a maximum value of $g_{\text{abs}} = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R) = -1.7 \times 10^{-2}$ at 470 nm. The value of g_{abs} varies somewhat with sample preparation and the highest value observed, amounts to -2.4×10^{-2} . The zero-crossing of the bisignate CD spectrum occurs at 417 nm, close to the absorption maximum. To complement the CD data, we measured the circular polarization of the luminescence (CPL) in ethanol. The CPL effect (Fig. 12) is expressed as the g -value of luminescence, which is defined as $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$. The g_{lum} value is found to be negative and essentially constant over the emission band between 570 and 640 nm ($g_{\text{lum}} = -0.5 \times 10^{-2}$). In this region the sign of g_{lum} is identical to the sign of g_{abs} at the high wavelength side (470 nm), but the magnitude of g_{lum} is less than of g_{abs} . The CD and CPL spectra are consistent with an exciton model in which two OPV7 molecules crystallize in the unit cell in a helical orientation. Such a helical orientation gives rise to a bisignate CD spectrum and a CPL effect with a sign corresponding to that of the high-wavelength CD band.²⁷ As mentioned, the absorption spectrum of the nanoparticles is characteristic of an H-aggregate and this indicates that the oligomers in the particle are (predominantly) oriented parallel. A simple model which could account for both the circular polarization and absorption data is one in which the angle between the two inequivalent molecules in the unit cell is small. Of the two Davydov levels arising in such a system, the higher level would carry most of the oscillator strength for the transition to and from the ground state. The absorption associated with the transition from the ground state to the lower Davydov level will be weak and may be obscured by effects of disor-

der and vibronic coupling. When the angle between the molecules is small the absorption spectrum will resemble that of H-aggregates. Circular dichroism spectroscopy is often more sensitive to weakly allowed transitions since the magnitude of the circular dichroic effect is determined by the product of electric and magnetic transition dipole moments.²⁸ Hence in CD and CPL the presence and influence of transitions involving the lower Davydov level are observed more clearly.

The reduction of the degree of circular polarization in emission compared to absorption can be explained in terms of luminescent trap sites.²⁹ In the region below 550 nm, i.e., within the absorption band of the OPV7 nanoaggregates, g_{lum} is positive. This is an artifact of the measurement because randomly polarized light originating from the remaining free molecules in solution is being absorbed by the nanoaggregates. Since g_{abs} of the nanoaggregates is negative in the 500–550 nm range, right circular polarized light will be preferentially absorbed by the sample and, hence, the emitted light exhibits positive g .

The UV/Vis and CD spectra of the nanoaggregates of OPV5–OPV7 change with increasing temperature in complex way. For the OPV7, e.g., warming up to 60 °C in isobutanol gives no significant change in the absorption, but causes a decrease of the CD signal by one order of magnitude. Above 95 °C, the UV/Vis absorption in isobutanol is almost identical to the spectrum in good solvents. Subsequent cooling, however, affords OPV7 assemblies different from the initial structures because both absorption and CD are different. These results indicate that at least two different types of the aggregates can be formed in a ratio that varies with the thermal history of the sample. Further research is necessary to elucidate the changes with temperature in more detail.

IV. CONCLUSIONS

The singlet excited state of the OPVns ($n=2-7$) has been investigated in solution at ambient and low temperature. At 295 K, the lifetime of the S_1 state decreases with chain length from 1.70 ns for OPV3 to 0.45 ns for OPV7 as result of an increase of radiative and nonradiative decay. The increase in radiative decay is consistent with the expected behavior on the basis of the Strickler–Berg relation. The increase in nonradiative decay can be explained by an enhanced intersystem crossing. Because the increase in nonradiative decay is much stronger, the photoluminescence quantum yield decreases for longer oligomers. At low temperature, vibronically resolved absorption and emission spectra have been obtained which enabled to determine the Huang–Rhys parameter and the relaxation energy in the excited state via a Franck–Condon analysis. Under these conditions the Stokes' shift is very small (≤ 0.04 eV). The Huang–Rhys parameter and relaxation energy of S_1 (0.165 ± 0.02 eV) is found to be only slightly dependent on conjugation length. The triplet state of the OPVns exhibits a $T_n \leftarrow T_1$ transition that evolves to lower energy with longer conjugation length. The lifetime of the triplet state is 3–8 ms. The relaxation energy of the T_n state is only 0.03 eV for OPV7, but increases significantly for the smaller oligomers. The OPVns with $n \geq 5$ readily form nanoaggregates in polar

solvents such as ethanol. The changes in absorption and emission in combination with the observed circular dichroism and circularly polarized emission indicate the formation of chiral H-type aggregates of the OPVns. In agreement with an exciton model, the chiral anisotropy factor in absorption (g_{abs}) is bisignate and at long wavelength of the same sign as the chiral anisotropy factor in emission (g_{lum}).

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