

# Spectroscopic studies of oligodiacetylenes in solution and polymer film†

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The photophysical properties of a series of monomeric, dimeric and trimeric oligodiacetylenes (ODAs; oligoenynes) bearing trimethylsilyl, *t*-butyl and *n*-octyl end-capping substituents were studied in solution and in a polymer film. Emission studies show a significant emission of oligodiacetylenes in solution, which increased with increased conjugation. This is remarkable given the near absence of fluorescence in oligoenynes of similar length (e.g. hexatriene) and polydiacetylenes (PDAs), which constitute the conjugation limit. A large Stokes shift was observed, and shown to originate from an energy difference between the Franck–Condon excited state and the fluorescent state. From near-identical angles obtained for the absorption and emission dipoles it was concluded that the overall geometry of ODAs does not significantly change upon electronic transition.

## Introduction

Organic materials containing extensive  $\pi$ -conjugation along a polymer backbone<sup>1–4</sup> frequently display opto-electronic characteristics that make them potentially useful materials for incorporation into devices,<sup>5,6</sup> including field-effect transistors (FETs),<sup>7–9</sup> and light-emitting diodes (LEDs).<sup>10,11</sup> Initially, studies of such materials were restricted to the electronic properties of  $\pi$ -conjugated polymers. In more recent years, however, the emergence of synthetic routes towards well-defined oligomers has opened up an additional route for the understanding and optimization of electro-optical properties of polymers. This oligomeric approach has already been successfully utilized to examine a number of  $\pi$ -conjugated materials that include oligothiophenes,<sup>3,12,13</sup> oligoarylenevinyls<sup>14</sup> and oligotriacetylenes.<sup>15,16</sup>

Polydiacetylenes (PDAs) are another class of these versatile materials;<sup>17–20</sup> a comprehensive review on PDAs has recently been published.<sup>21</sup> Due to their topochemical, solid-state polymerization, PDAs are necessarily highly ordered, with significant  $\pi$ - $\pi$ -interactions between adjacent PDA chains. The combination of length and polarizability of PDA chains also allows significant  $\pi$ - $\pi$ -interactions in solution, especially in non-polar, aprotic solvents.

Despite a large number of studies of PDAs (>2500 since 1990) still relatively little is known about the geometry and nature of excited state PDAs. The lifetimes of electronically excited PDAs are typically in the order of picoseconds at room temperature.<sup>22</sup> Because of this time scale of nonradiative decay, alternative radiative decay processes are usually not important, and bulk PDAs do, in contrast to several other conjugated materials, not yield any appreciable fluorescence (typical fluorescence quantum yields are smaller than  $10^{-3}$ ).<sup>23</sup>

Some exceptions are known, and these include weak fluorescence in some red-phase PDAs,<sup>24</sup> and in isolated PDA chains in their monomer matrix.<sup>23</sup>

The present paper presents a study of the photophysics of oligomers of polydiacetylenes, to delineate in more detail the excited state properties of repeating enynic units ( $-\text{C}=\text{C}-\text{C}\equiv\text{C}-$ ). There are only a few accounts in the literature in which oligodiacetylenes (ODAs) have been synthesized and characterized.<sup>25–31</sup> The UV-Vis spectra of these ODAs show red-shifted absorption and larger extinction coefficients with increasing conjugation length.<sup>25,26</sup> However, little—one communication about only one oligomer—has been reported about the fluorescence behavior of ODAs.<sup>32</sup> The limited photophysical data currently available for ODAs in solution made it interesting to synthesize a series of ODAs and study their photophysical behavior, in an attempt to gain further insight into the photophysics of PDAs.

In the present paper we report on the effects of substituents and extended conjugation on the absorption and emission behavior of ODAs (up to trimeric species) in solution and in polymer films, as well as on the direction of the absorption and emission dipoles of ODAs. These directions are of interest, as they provide information about a possible change in the molecular geometry between the ground and excited states. To these aims the following ODAs were synthesized and studied (Fig. 1).<sup>28</sup>

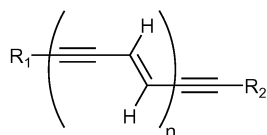
## Results and discussion

### Absorption and steady state fluorescence in solution

Typical absorption spectra with two characteristic bands for near-equimolar solutions of **1b**, **2b** and **3b** in *n*-hexane are presented in Fig. 2. Detailed photophysical data are shown in Table 1.

Both the observed increase of extinction coefficient ( $\epsilon$ ) and red-shifting of the absorption band with increasing number of repeating enynic units are in agreement with enhanced

† Electronic supplementary information (ESI) available: Fig. 1: Experimental and fitted curves of total fluorescence decay (left) and fluorescence anisotropy decay (right) of **3c** measured at 303 K in *n*-hexane solution. See <http://www.rsc.org/suppdata/cp/b4/b412556h/>



- 1  $n = 1$  a:  $R_1 = R_2 = \text{CMe}_3$       b:  $R_1 = \text{CMe}_3, R_2 = \text{SiMe}_3$   
 c:  $R_1 = R_2 = \text{SiMe}_3$       d:  $R_1 = n\text{-C}_8\text{H}_{17}, R_2 = \text{SiMe}_3$   
 e:  $R_1 = R_2 = n\text{-C}_8\text{H}_{17}$
- 2  $n = 2$  a:  $R_1 = R_2 = \text{CMe}_3$       b:  $R_1 = \text{CMe}_3, R_2 = \text{SiMe}_3$   
 c:  $R_1 = R_2 = \text{SiMe}_3$       d:  $R_1 = n\text{-C}_8\text{H}_{17}, R_2 = \text{SiMe}_3$   
 e:  $R_1 = R_2 = n\text{-C}_8\text{H}_{17}$
- 3  $n = 3$  a:  $R_1 = R_2 = \text{CMe}_3$       b:  $R_1 = \text{CMe}_3, R_2 = \text{SiMe}_3$   
 c:  $R_1 = R_2 = \text{SiMe}_3$       d:  $R_1 = n\text{-C}_8\text{H}_{17}, R_2 = \text{SiMe}_3$   
 e:  $R_1 = R_2 = n\text{-C}_8\text{H}_{17}$

Fig. 1 Oligodiacyetylenes (ODAs) under present study.

$\pi$ -conjugation.<sup>25,26</sup> Only a minor effect (0.06 eV) of solvent polarity on the absorption spectra is observed when changing the solvent from *n*-hexane to toluene (data not shown). This is similar to data reported for *iso*-PDA oligomers (0.04 eV) for a variety of solvents.<sup>33</sup> However, it is significantly smaller than reported for PDAs (0.11 eV).<sup>34</sup> This is analogous to the findings for polyenes and can be explained from the expression for the decrease  $h(\nu - \nu_0)$  in the excitation energy caused by the interaction of a nonpolar solute with a collection of nonpolar solvent molecules:

$$h(\nu - \nu_0) \propto \frac{1}{V} \frac{n^2 - 1}{n^2 + 2} (M_{\text{eg}}^2 - E(\alpha_g - \alpha_e)) \quad (1)$$

in which  $V$  is the effective solute cavity volume,<sup>35</sup>  $n$  is the refractive index,  $M_{\text{eg}}$  is the electric dipole transition moment for the solute,  $E$  is the mean excitation energy of the solvent and the  $\alpha$ 's are polarizabilities of the solute in the ground and excited states, respectively.<sup>36</sup> Cumulatively, this effect is more pronounced for the highly absorbing PDAs, leading to a larger solvatochromic shift than for ODAs.

Small substituent effects on the absorption spectra are evident from the red-shifting and higher  $\epsilon$  values for ODAs with the electron-donating trimethylsilyl (TMS) moiety relative to alkyl substituents (Table 1). Similar red-shifting of absorption maxima is observed in phenylenevinylene<sup>37</sup> and oligotriacyetylene<sup>16</sup> derivatives upon introduction of electron-donating substituents, while introduction of electron-withdrawing groups in carotenoid derivatives<sup>38</sup> and distyrylbenzenes<sup>39</sup> results in blue-shifting. Calculation of the energies required for

Table 1 Wavelengths of maximum absorption ( $\lambda_1$  and  $\lambda_2$ ), corresponding extinction coefficients ( $\epsilon$ ), and wavelengths of the (0–0) fluorescence band for various ODAs in *n*-hexane

ODA	Absorption maxima				Flu(0,0) $\lambda_{\text{f}}/\text{nm}$	$\Phi_{\text{F}}^a$ ( $\times 10^{-4}$ )	Stokes shift $\Delta\lambda/\text{eV}$
	$\lambda_1/\text{nm}$	$\epsilon_1^b$	$\lambda_2/\text{nm}$	$\epsilon_2^b$			
1a	262	2.9	276	2.9	—	5	—
1b	269	3.1	284	3.2	—	3	—
1c	273	3.4	289	3.8	—	2	—
1d	269	3.0	284	3.1	—	4	—
1e	263	2.7	277	2.8	—	—	—
2a	313	4.5	334	5.1	371 <sup>c</sup>	16	0.37
2b	316	4.1	338	4.7	373 <sup>c</sup>	24	0.34
2d	316	4.5	338	5.0	370 <sup>c</sup>	25	0.32
3a	350	2.7	375	2.5	425 <sup>d</sup>	220	0.39
3b	353	5.3	377	5.7	429 <sup>e</sup>	79	0.40
3c	354	6.2	380	5.7	435 <sup>e</sup>	110	0.41
3e	349	4.1	375	3.7	425 <sup>d</sup>	210	0.39

<sup>a</sup> Fluorescence quantum yields determined using tryptophan as reference. <sup>b</sup>  $\times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . <sup>c</sup>  $\lambda_{\text{EX}} = 336 \text{ nm}$ . <sup>d</sup>  $\lambda_{\text{EX}} = 375 \text{ nm}$ . <sup>e</sup>  $\lambda_{\text{EX}} = 380 \text{ nm}$ .

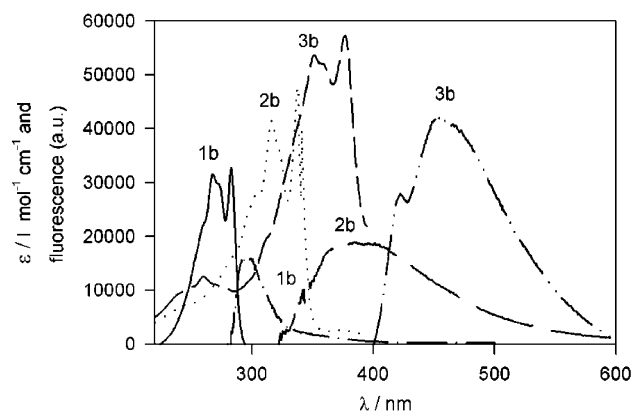


Fig. 2 Absorption and fluorescence spectra of near-equimolar ( $2 \times 10^{-6} \text{ M}$ ) solutions of ODAs **1b**, **2b** and **3b** in *n*-hexane. (The fluorescence spectra of **1b** and **2b** have been multiplied by a factor of 5.)

excitation of the symmetrical oligomers **a** and **c** to the first excited singlet state reproduces this trend.<sup>40</sup>

Fluorescence spectra are shown in Fig. 2 for **1b**, **2b** and **3b** at near-equimolar concentrations in *n*-hexane (fluorescence quantum yields are given in Table 1). The fluorescence of most monomeric compounds under study is weak, and fluorescence is not clearly observable in **1e**. The fluorescence intensity increases for the dimeric compounds and again for the trimeric compounds. In the spectra of **2b** and **3b** a shoulder at the high-energy side of the fluorescence band is clearly visible and is considered to be the maximum of the (0–0) transition. For the monomeric oligomers the (0–0) transition cannot be resolved. To the best of our knowledge, the only other data on *both* absorption and emission spectroscopy of an ODA were published for **3a** at 77 K in 3-methylpentane, with a fluorescent quantum yield  $\Phi_{\text{F}} = 0.01$  reported (our data for **3a**:  $\Phi_{\text{F}} = 0.022$  at 298 K; see also under lifetime studies).<sup>32</sup>

The electron-donating TMS substituents lead to slightly longer wavelengths of emission relative to alkyl groups, but do hardly influence the fluorescence quantum yields. Similar substituent effects have been reported for the emission of diphenylhexatrienes in toluene.<sup>41</sup> The values for fluorescence quantum yields are, however, significant when compared with analogous data for PDAs. PDAs show little, if any, fluorescence, with typical values from 0 to  $< 10^{-3}$ ,<sup>21,23</sup> although the emission has been shown to be dependent upon the nature of substituents present. A high value of *ca.*  $10^{-2}$  has been reported (in benzene,  $\lambda_{\text{EX}} = 480 \text{ nm}$ ) for an *N*-carbazolyl substituted PDA.<sup>42</sup> This value is, however, still lower than for the corresponding data reported for the trimeric ODAs studied here.

The oligoynes under study display a somewhat different fluorescence than related oligoynes  $\text{R}(\text{CH}=\text{CH})_n\text{R}'$  and oligotriacyetylenes  $\text{R}(\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})_n\text{R}'$ . Butadiene and hexatriene are practically non-fluorescent,<sup>43</sup> which should be compared to the weak but clearly observable fluorescence of *e.g.* **1b**. Linear polyenes having four or more double bonds are only very weakly fluorescent, *e.g.* tetradecaheptaene has a quantum yield of only 0.001.<sup>44</sup> This should be compared to **3b**, which has a comparable conjugation length but fluoresces about one order of magnitude better. Oligotriacyetylenes (repeating unit:  $[\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}]_n$ ) only display fluorescence for its dimeric and trimeric oligomers ( $\Phi_{\text{F}} = 0.01$ ), while for higher chain lengths fluorescence is quenched.<sup>45,46</sup> Interestingly, ODA emissions thus are larger than that of both comparable  $[\text{CH}=\text{CH}]_n$  and  $[\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}]_n$  structures, while one might have expected it to be intermediate ( $[\text{CH}=\text{CH}-\text{C}\equiv\text{C}]_n$  in between  $[\text{CH}=\text{CH}]_n$  and  $[\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}]_n$ ).

The absorption and fluorescence data in Table 1 reveal relatively large Stokes shifts for dimeric and trimeric ODAs in *n*-hexane [data in chloroform—not shown—are very

similar]. A Stokes shift of 0.39 eV for **3a** at 298 K was obtained, compared to 0.21 eV reported previously at 77 K.<sup>32</sup> The (0–0) fluorescence of monomeric ODAs **1a** and **1c** is not clearly resolved. However, by using the slight shoulder evident at the left portion (high energy side) of their emission spectra as reference for a (0–0)-transition, a gradual increase in Stokes shift values can be discerned in going from the monomer *via* the dimer to the trimer. A steady-state absorption and fluorescence study on films of the trimer showed even larger Stokes shifts.<sup>47</sup> It would be of significant interest to study the absorption and emission behavior of even longer ODAs to evaluate the effect of increasing conjugation on Stokes shift values and fluorescence quantum yields, and such studies are presently on-going.

The Stokes shifts may originate from (a) charge transfer (CT)-mixing in the excited state, from (b) a relatively large geometry change in going from the ground state to the excited state (*i.e.* significant rotations or changes in the overall geometrical symmetry), or from (c) energy difference between the Franck–Condon excited state and the fluorescent state. A set of experiments was performed to differentiate between these possibilities.

It is easy to discard option (a), as the Stokes shift is nearly identical in both *n*-hexane and chloroform, which makes the involvement of CT unlikely. The distinction between options (b) and (c), however, is more complicated (*vide infra*).

### Fluorescence lifetimes

The fluorescence lifetimes of the trimeric ODAs **3a**, **3c** and **3e** were measured in *n*-hexane solutions, and range from 0.53 ns to 0.84 ns, depending on both substitution pattern and temperature (Table 2). The observed lifetimes for **3a** display a linear relationship with temperature. An—admittedly rather extended—linear extrapolation of lifetime *vs.* temperature for **3a** to 77 K affords a lifetime of 1.4 ns, which is consistent with a reported value of  $1.49 \pm 0.05$  ns at 77 K.<sup>32</sup> The sensitivity of the emission to electronic substituents is evident from the lower average fluorescence lifetimes for ODAs bearing TMS substituents. From the quantum yield ( $\Phi_F$ ) and the fluorescence lifetime ( $\tau_F$ ) the natural fluorescence lifetime ( $\tau_F^0$ ) can be calculated, using

$$\tau_F^0 = \frac{\tau_F}{\Phi_F} \quad (2)$$

Results are shown in Table 3. Using the Strickler–Berg relationship (eqn. (3))<sup>48,49</sup> analogous to Hudson and Kohler,<sup>43</sup> the natural lifetime can also be calculated from the emission and

**Table 2** Estimated fluorescence and anisotropy decay parameters of compounds **3a**, **3c** and **3e** measured at three different temperatures in *n*-hexane

ODA	<i>T</i> /K	$\tau$ /ns	$\tau_R$ /ns	$r_0$	$\phi^{  \alpha}$
<b>3a</b>	283	0.823	0.226	0.32	15.4
	293	0.794	0.188	0.313	16.1
	303	0.768	0.159	0.312	16.2
<b>3c</b>	283	0.55	0.167	0.29	18.3
	293	0.541	0.125	0.327	14.6
	303	0.526	0.108	0.325	14.9
<b>3e</b>	283	0.835	0.125	0.356	11.2
	293	0.813	0.111	0.339	13.3
	303	0.786	0.010	0.332	14.1

<sup>a</sup> ODAs **3a** and **3c** do not orient fully within the polyethene film and  $\phi_{\text{abs}}$  could hence not be determined. However, for **3e**  $\phi_{\text{abs}} \approx \phi_{\text{em}}$  and we assume that the same holds true for **3a** and **3c**, and thus  $\phi$  was calculated using  $r_0 = 0.1(3\cos^2\phi_{\text{abs}})(3\cos^2\phi_{\text{em}}) = 0.1(3\cos^2\phi - 1)^2$

**Table 3** Fluorescence quantum yields  $\Phi_F$ , and experimental ( $\tau_F^0$ ) and calculated ( $\tau^0$ ) natural fluorescence lifetimes

ODA	$\Phi_F (\times 10^{-4})$	$\tau_F^0$ /ns	$\tau^0$ /ns
<b>3a</b>	220	36	4.8
<b>3c</b>	110	49	2.0
<b>3e</b>	210	39	3.0

absorption spectra, in which  $n$  equals the refractive index,  $\int F(\nu)d\nu$  is the integrated emission spectrum in wavenumbers and  $\int \epsilon d\nu$  is the integrated absorption spectrum.

$$\frac{1}{\tau^0} = k_F = 2.88 \times 10^{-9} n^2 \frac{\int F(\bar{\nu})d\bar{\nu}}{\int \bar{\nu}^{-3} F(\bar{\nu})d\bar{\nu}} \int \frac{\epsilon d\bar{\nu}}{\bar{\nu}} \quad (3)$$

This relation is valid when the transition is strongly allowed ( $\epsilon \geq 8000$ ), when the geometry in the excited state does not change much and when the Franck–Condon excited state is the same as the fluorescent state.<sup>48,50,51</sup> The results are shown in Table 3. In all cases  $\tau_F^0 \gg \tau^0$ , indicating that either there is a large geometry change upon excitation (option b), or that there is an energy difference between the Franck–Condon excited state and the fluorescent state (option c). This is in line with the observed Stokes shift to a lower energy of emission.

For PDAs it is proposed that the geometry of the ground state is an enynic structure and that of the lowest excited state a butatrienic structure (Fig. 3).<sup>22</sup> On the other hand, Raman studies of an *N*-carbazolyl-substituted PDA displayed no significant differences between ground- and excited-state C=C and C≡C stretching frequencies, suggesting that the geometry of the excited polymer is not substantially different from that in the ground state.<sup>42</sup> These contrasting conclusions warranted a further study of the excited state geometry of ODAs. In order to study this, polarized absorption<sup>52–55</sup> measurements were performed on ODAs in oriented films of polyethene, and time-resolved fluorescence anisotropy measurements on ODAs in *n*-hexane solution. Using these techniques it is possible to obtain information about the angle between the transition dipole moments (absorption and emission, respectively), and the longitudinal axis of conjugated molecules.

### Polarized absorption of ODAs in oriented polymer films

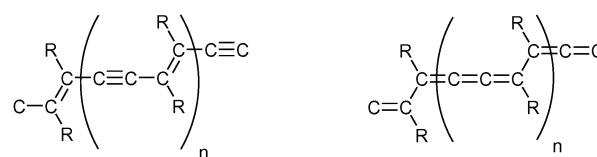
The absorption spectrum of **3c** in a polyethene film was qualitatively similar in structure to that of **3c** in *n*-hexane, and no red-shifting in the absorption maximum was observed.

Polarized absorption spectra for films of **3c**, obtained by soaking a polyethene substrate in a solution of **3c** in chloroform, from chloroform onto polyethene substrate were measured at various stretch factors. Both horizontal and vertical polarized spectra showed maximum absorptions at the lowest stretch factor.

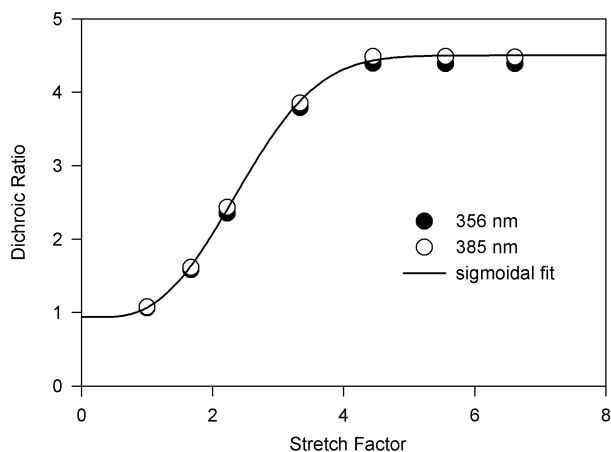
For oriented chromophores in stretched polymer films the angle,  $\langle \phi \rangle$ , between the transition dipole moment and the longitudinal axis can be determined by measuring the dichroic ratio,  $R_d$ :

$$R_d = A(\alpha = 0)/A(\alpha = 90) \quad (4)$$

in which  $A(\alpha)$  is the absorption for an angle  $\alpha$  between polarization direction and stretch/orientation axis.



**Fig. 3** The enynic structure of the ground state (left) and the butatrienic structure of the excited state of PDAs (right).



**Fig. 4** Experimental dichroic ratios ( $R_d$ ) (● at 356 nm and ○ at 385 nm) and sigmoidal fit for **3c** as a function of the stretch factor.

Experimental values of  $R_d$  as determined for the ODAs in a polyethene film for different stretch factors are plotted vs. stretch factor in Fig. 4. The value of  $R_d$  increases with increasing stretch factor until a plateau is reached, beyond which no further increase in  $R_d$  is observed. After fitting the results to a Weibull sigmoidal function, a value is obtained for  $R_d$  at infinite stretch,  $R_d(\infty)$ , from which  $\phi$  can be determined.<sup>56</sup>

$$\cos\phi = \pm \sqrt{[R_d(\infty)/(2 + R_d(\infty))]} \quad (5)$$

For oligomers **1e** and **3e**,  $R_d(\infty)$  and the corresponding value of  $\phi$  are given in Table 4. No change in  $R_d$  was observed for the monomeric ODAs **1a**, **1b** and **1c** upon increasing the stretch factor, suggesting that the axial ratio is too small to orient the molecules by stretching of the polyethene film. However, substitution with *n*-octyl chains, as in compound **1e**, enabled orientation of a monomer. For trimeric oligomers partial orientation was achieved for the TMS and *t*-butyl substituted derivatives **3a** and **3c**. Maximal orientation was again obtained for an octyl-substituted derivative, affording the highest value of  $R_d(\infty)$  for **3e**. From these values of  $R_d$  the angle  $\phi$  was determined. For the monomer **1e**  $\phi \approx 24^\circ$  is somewhat larger than that found for the trimer **3e** ( $\phi \approx 14^\circ$ ).

The  $C_{2h}$  symmetry of the conjugated system of the ODAs under study (ODAs **a**, **c** and **e**) implies a transition dipole moment in the molecular plane, but does not enforce the transition moment to be co-linear with the molecular longitudinal axis. Our results reveal the presence of a small angle ( $24^\circ$  and  $14^\circ$  for **1e** and **3e**, respectively) between the transition moment and the longitudinal axis, which seems to decrease with increasing conjugation. Both the small deviation from parallelism<sup>57</sup> and the decreasing angles with increasing conjugation have also been found for polyenes with  $C_{2h}$  symmetry.<sup>58</sup> These phenomena therefore seem to be independent of the particular chromophore under study, but rather depend on the overall geometrical symmetry of the conjugated system, although no symmetry restrictions enforce them. Comparison of these absorption transition dipole moments with the emission transition dipole moments can now determine whether a large geometry change is involved between absorption and

emission for ODAs, *i.e.* whether this option (b) is operative in causing the observed Stokes shift.

### Fluorescence anisotropy of trimeric ODAs in solution

Time-resolved fluorescence anisotropy measurements were used to follow the depolarization ( $r$ ) of the fluorescence of **3a**, **3c** and **3e** during rotation of the molecules in solution. This method allows for the determination of the transition dipole moment.<sup>59</sup> Assuming the molecules under study have a rod-like shape (relatively large axial ratio), rotation of the molecules around the longitudinal axes is extremely fast compared to that around the short axis. Because of the picosecond time-resolution in our experimental set-up, the anisotropy therefore will apparently decay with a single exponent:

$$r(t) = r_0 \exp(-t/\tau_R) \quad (6)$$

with

$$r_0 = 0.1(3\cos^2\phi_{\text{abs}} - 1)(3\cos^2\phi_{\text{em}} - 1) \quad (7)$$

in which  $\phi_{\text{abs}}$  and  $\phi_{\text{em}}$  are the angles that the absorption and emission dipoles make with the longitudinal axis, respectively,  $r_0$  is the initial anisotropy of the system and  $\tau_R$  is the rotational correlation time. The estimated mean  $r_0$  values are all smaller than 0.4, which is the theoretical value for a single rotating dipole in an isotropic solution having the transition moments of absorption and emission co-linear and parallel with the longitudinal axis.<sup>60</sup> These reduced  $r_0$  values are a consequence of the limited time-resolution of the laser set-up with which we were not able to detect an initial decrease from 0.4, due to rapid rotation around the longitudinal axis.

From the stretching experiments it was derived that  $\phi_{\text{abs}} = 14^\circ \pm 1^\circ$  for **3e**. Substituting the values of  $r_0$  and  $\phi_{\text{abs}}$  into eqn. (7) yields  $\phi_{\text{em}}$  to be  $13^\circ \pm 1^\circ$ . The fact that the values of  $\phi_{\text{abs}}$  and  $\phi_{\text{em}}$  are quite similar implies that the overall shape of the ODA molecules—apart from bond length changes and perhaps small angle changes—do not change upon excitation in solution. In other words: explanation (b) for the Stokes shift (“large geometry change between Franck–Condon excited state and fluorescent state”) is likely incorrect, and the large Stokes shift is explained from different absorbing and emitting states (option c).

As a result the overall picture of the lower excited states seems to be as follows: Electronic excitation proceeds to a  $B_u$  state. Lower than this state a state with gerade symmetry is found, from which fluorescence occurs. For the trimer and larger molecules<sup>2,40</sup> this  $g$  state is an  $A_g$  state. The energy difference between the  $B_u$  and  $A_g$  state causes the large Stokes shift. The  $A_g$  state has an overall geometry that is rather similar to the  $B_u$  state. Given the fluorescence lifetimes (on the order of a nanosecond), there is likely an energy barrier for geometrical distortions to any lower energy conformer that would lead to radiationless decay. This is similar to the situation observed and calculated for oligoenes of a similar symmetry (trienes, pentaenes, heptaenes, *etc.*), in which the minimum energy conformation of the excited states ( $90^\circ$  rotation around a C=C bond) can only be reached after crossing an energy barrier.<sup>61</sup> To further clarify the nature of the excited states of PDAs, the synthesis of longer ODAs and their photophysical properties are presently under study.

### Conclusions

A systematic study was made of the absorption and emission characteristics of a series of monomeric, dimeric and trimeric oligodiacylenes (ODAs) bearing TMS and/or alkyl end-capping substituents. Specifically, the increased fluorescence quantum yields with increasing conjugation is of interest, in view of the weak to absent fluorescence with the even more extended conjugation present in polydiacylenes (PDAs). Significant

**Table 4** Angles between the absorption dipole moment and the longitudinal axis of **1e** and **3e**

ODA	$R_d(\infty)$ ( $\lambda_1$ )	$R_d(\infty)$ ( $\lambda_2$ )	$R_d(\infty)$ (average)	$\phi/^\circ$
<b>1e</b>	$10.0 \pm 0.3$	$9.8 \pm 0.1$	$9.9 \pm 0.2$	$24 \pm 1$
<b>3e</b>	$28.9 \pm 0.6$	$36 \pm 0.9$	$32 \pm 4$	$14 \pm 1$

Stokes shifts (up to 0.39 eV) are observed, which are attributed to the non-absorbing nature of the lowest excited state (of gerade symmetry). From polarized absorption and time-resolved fluorescence depolarization measurements, it was shown that the transition dipole moments for absorption and emission were parallel within the experimental error, and to decrease with increasing conjugation (24° for monomers; 14° for trimers). The parallel absorption and emission transition dipole moments indicate that the overall shape of the molecules does not change significantly upon electronic transition. In combination with the large Stokes shift, this provides support for electronic excitation towards a  $B_u$  state, and fluorescence from a lower-lying  $A_g$  state that is not very different in geometry from the  $B_u$  state.

## Experimental details

### Steady-state absorption and fluorescence of ODAs in *n*-hexane

Absorption spectra of the oligomers in hexane a.r. (Aldrich) were recorded using a Cary 5E UV-Vis-NIR spectrophotometer (scan range 600–190 nm, SBW 2 nm, scan rate 300 nm min<sup>-1</sup>, data interval 0.5 nm) and steady state fluorescence spectra in *n*-hexane a.r. (Aldrich) were recorded on a Fluorolog-322 (slit exc.: 5 nm, slit em.: 5 nm, scan rate: 120 nm min<sup>-1</sup>, data interval 0.5 nm) with the right angle mode.

### Determination of fluorescence quantum yields of ODAs in solution

In order to evaluate the fluorescence quantum yields ( $\Phi_F$ ) of the ODAs in *n*-hexane, the areas of the corrected emission spectra were compared with that of a reference molecule. A dilute solution of tryptophan in water was used, and a value of  $\Phi_F = 0.13$  was obtained at 25 °C, measured at 280 nm. The relevant fluorescence quantum yields of the ODAs were then determined from the relationship.<sup>60</sup>

$$\Phi_F = \Phi_r \frac{I \text{ OD}_r n^2}{I_r \text{ OD} n_r^2} \quad (8)$$

where  $I$  and  $I_r$  are the integrated fluorescence intensities of the ODA and tryptophan solutions, respectively, OD refers to the optical densities of the respective solutions, and the last term accounts for the different refractive indices of the two solvent media.

### Direction of the transition dipole moment of the oligomers in polyethene films

The oligomers were absorbed in polyethene film by allowing the films to soak for 2–3 d in a concentrated solution of the oligomers in chloroform (HPLC-grade, Lab-scan). The concentrations of the ODAs were ca. 70 mM. The films were slowly stretched with a rack until a stretch factor of 5 was reached. The absorption was recorded with vertical and horizontal polarized light at different stretch factors using a Cary 5E UV-Vis-NIR spectrophotometer (scan range 600–230 nm, SBW 5 nm, scan rate 300 nm min<sup>-1</sup>, data interval 0.5 nm), and Harrick polarizers. After this the dichroic ratio,  $R_d$ , was calculated at different stretch factors, and fitted with Sigma-Plot. The angle between the transition moment and the length-axis of the molecules was correlated with the dichroic ratio at infinite stretch factor.

### Lifetime of fluorescence and fluorescence anisotropy of trimeric ODAs in solution

Total fluorescence decay curves of *n*-hexane solutions of **3a**, **3c**, and **3e** were recorded and fitted to an exponential function. The quality of the fit was judged by the  $\chi^2$  statistical criterion

and by visual inspection of the time dependence of weighted residuals, and their auto-correlation functions (see ESI† for data for **3c**). The fluorescence lifetimes, which were calculated from the decay component with which 99% of the time-integrated fluorescence signal could be fitted, are presented in Table 2, together with the rotational correlation times ( $\tau_R$ ) and the initial anisotropy values ( $r_0$ ) that were estimated from the fitted polarized fluorescence decays.

### Time-resolved fluorescence measurements

Conditions and set-up as reported earlier by Novikov *et al.*<sup>62,63</sup>

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