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Liquid Crystals

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Fluorescent columnar liquid crystalline 3,4,9,10-tetra-(n-alkoxycarbonyl)-perylenes

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Fluorescent columnar liquid crystalline 3,4,9,10-tetra-(*n*-alkoxycarbonyl)-perylenes

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The title compounds were recently demonstrated to be useful as luminescent electron transport materials in organic light emitting diodes. Here, we present studies of the fluorescence of the homologues with chain lengths between 2 and 10 carbon atoms. Dilute solutions of the investigated compounds show absorption in the range between 410 and 490 nm and fluorescence between 475 and 555 nm. However, the columnar phase of the pure compounds exhibits fluorescence at considerably larger wavelength (550–650 nm) and gives larger fluorescence lifetimes. This behaviour can be explained by the formation of excimers in the mesophase. The phase transitions to the liquid crystal state are associated with a distinct change of the fluorescence intensity.

1. Introduction

The development of organic light emitting diodes (OLEDs) has made considerable progress during the last thirteen years. Due to the development of both low molecular mass materials and polymers with high charge carrier mobility, the performance of OLEDs has been improved to a quality which allows the commercial production of large area displays. In the early works [1, 2], electroluminescence in anthracene could be demonstrated, but the required voltages were very high (> 100 V) and the brightness was poor. However, considerable improvements were achieved using a double layered structure of an aromatic diamine as hole transporter and a luminescent complex with electron transporting properties [3], or systems based on conjugated polymers, e.g. poly(*p*-phenylenevinylene), PPV [4]. Not only the development of highly conjugated organic materials, but also the construction of more sophisticated multilayer systems helped to increase the effectiveness of OLEDs [5–9]. In order to make sure that the recombination of electrons and holes leads to the emission of light, it is necessary to restrict the position of the recombination events to a thin layer containing the fluorescent chromophore. A useful set-up for this purpose is a three-layer arrangement consisting of a hole transporting organic layer, a dye-doped layer, and an electron transporting organic layer. Examples of good electron transporting layers are aluminium chelates [3], oxadiazole derivatives [10], or poly(phenylquinoxalines) [11]. Additional injection layers may be useful in order to reduce the threshold voltages [7].

Recently, it has been demonstrated that liquid crystals are particularly useful for the construction of organic light emitting diodes [12–15]. It is well known that columnar liquid crystals have a large potential as hole transporting layers. The charge carrier mobility, e.g. $\mu \approx 1\text{–}5 \times 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in the columnar mesophase and $\approx 10^{-1}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in a highly ordered helical columnar phase of an electron-rich columnar triphenylene derivative, is much higher than the values for amorphous organic materials and only slightly lower than the respective values for molecular single crystals [16]. A considerable advantage of columnar liquid crystals is their ability to expel defects in an annealing process [13, 14]. It was thus our aim to develop columnar liquid crystals with electron transport capability, to complement the known columnar hole transporters. We replaced the electron donating alkoxy substituents of the known columnar transport materials by electron withdrawing alkoxycarbonyl side chains. As aromatic core, we chose to use perylene in view of the intense fluorescence of its derivatives.

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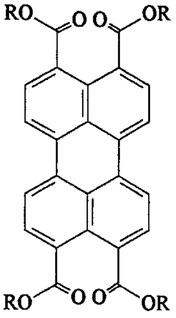
We report here our experimental results on the homologous series of 3,4,9,10-tetra-(*n*-alkoxycarbonyl)perylenes $C_{20}H_8(CO_2(CH_2)_{n-2}CH_3)_4$.



$R = C_nH_{2n+1}$

These compounds are not new [17], but their liquid crystalline properties had not been noted previously. The central unit is the chromophore of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) which was extensively studied in previous work related to OLEDs [9]. However, our compounds show not only fluorescence similar to PTCDA, but also the ability to form liquid crystalline phases. Due to the latter property, a bilayer OLED was constructed recently where both organic layers are made of liquid crystals [18]. Here, we present details of the phase behaviour and the fluorescence of these useful compounds.

2. Experimental

The $n = 2$–10 homologues of the series of 3,4,9,10-tetra-(*n*-alkoxycarbonyl)perylenes were prepared in 30–60% yield by refluxing 2 g of perylene-3,4,9,10-tetracarboxylic dianhydride with 10 g of potassium carbonate in 50 ml of alkyl tosylate ($n = 2$), alkyl iodide ($n = 3$–5) or alkyl bromide ($n = 6$–10) for two days ($n = 2, 7$–10) or one week ($n = 3$–6) (the reaction time depends on the boiling point of the halogenide or tosylate), followed by column chromatography (silica gel/1 : 2 chloroform/ethyl acetate) and threefold recrystallization from ethanol. ^{1}H NMR of the ethyl derivative (200 MHz, $CDCl_3/(CH_3)_4Si$): δ (ppm) = 1.46 (t, 12H, $J = 7$ Hz), 4.41 (q, 8H, $J = 7$ Hz), 7.82 (d, 4H, $J = 8$ Hz), 7.85 (d, 4H, $J = 8$ Hz).

In order to determine their transition temperatures, the substances were studied by polarizing optical microscopy, and the temperature dependence of the heat capacity was measured using differential scanning calorimetry (DSC7, Perkin-Elmer). We recorded the absorption and fluorescence spectra of both the pure compounds and dilute solutions in chloroform (p.a.). In the latter case, the concentration of the dye was approximately 1×10^{-5} mol × l^{-1}, and 1 cm quartz cells were used. In order to study the pure compounds in the crystalline, liquid crystalline and isotropic liquid states, we prepared rather thin cells containing a dye layer with a thickness of a few microns between quartz plates (∅ 12 mm). Prior to the cell preparation, the quartz substrates were cleaned in an ultrasonic bath for 15 min using acetone. Subsequently, the requisite substance was sandwiched between the two substrates. The resulting sample was heated to the isotropic state, and was then cooled slowly to room temperature. The absorption and fluoresence spectra were recorded by means of Perkin-Elmer spectrophotometers, models Lambda 19DM, and MPF4, respectively. In addition, we measured the lifetime of the excited states using a fluorescence photometer equipped with a UV flash light and time-resolved single photon counting detection. In addition to cells with homeotropic alignment, we investigated samples where the columns were oriented parallel to the quartz plates. The latter samples were prepared by shearing the columnar phase between the two substrates.

3. Results and discussion

The 3,4,9,10-tetra-(*n*-alkoxycarbonyl)perylenes investigated have the typical molecular structure of discotic liquid crystals: a rigid aromatic core and several lateral alkyl chains. If an isotropic sample of one of these compounds is cooled slowly from the isotropic state into the mesomorphic temperature range, a star-like texture can be seen in the polarizing microscope which is typical for columnar hexagonal liquid crystals (figure 1).

The clearing points (figure 2, table 1) decrease with increasing chain length from 313°C ($n = 2$) to 100°C ($n = 9$). Only the longest homologue with $n = 10$ shows no liquid crystalline phase.

The existence of a columnar phase is confirmed by X-ray powder diffraction experiments. The latter indicate a roughly temperature independent distance of 1.5 to 2.0 nm between the columns (figure 3) in the liquid crystalline state.

For comparison, the spatial periodicities corresponding to the main small angle diffraction peaks of the solid phase at room temperature are also given in figure 3.

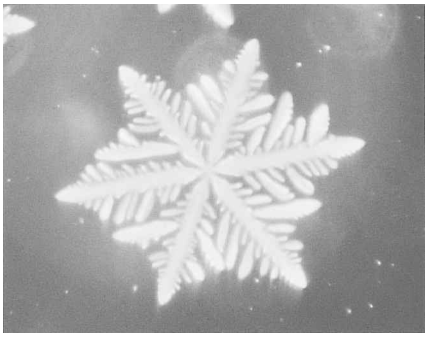


Figure 1. Coexistence of the isotropic and the columnar phase ($n = 8$).

Table 1. Transition temperatures and transition enthalpies of the tetra-alkyl perylenetetracarboxylates.

n	Transition temperatures (°C) and enthalpies ($J\,g^{-1}$) in brackets
2	solid 134 (16) solid 150 (5) solid 244 (3) Col_{hex} 313 (19.5) I
3	Cr 193 (66) Col_{hex} 287 (11.5) I
4	Cr 161 (68) Col_{hex} 242 (6.1) I
5	Cr 114 (73) Col_{hex} 203 (3.8) I
6	Cr 72 (58) Col_{hex} 177 (3.5) I
7	Cr 63 (78) Col_{hex} 152 (2.6) I
8	Cr 62 (29) Col_{hex} 132 (2.3) I
9	Cr_1 44 (35) Cr_2 60 (28) Col_{hex} 100 (1.4) I
10	Cr 51 (24) I

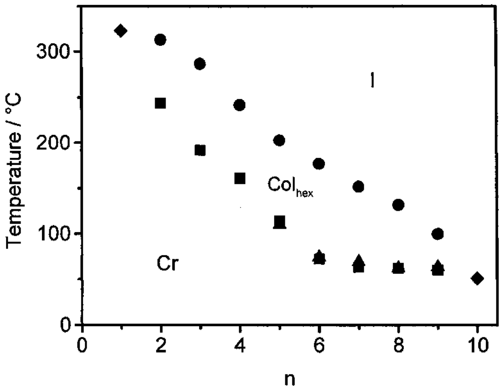


Figure 2. Transition temperatures of the homologues: (●) clearing temperature (DSC); (■) melting temperature (DSC); (▲) melting temperature obtained from fluorescence data. The $n = 1$ and $n = 10$ homologues show no mesophase, giving a solid to isotropic liquid transition (◆).

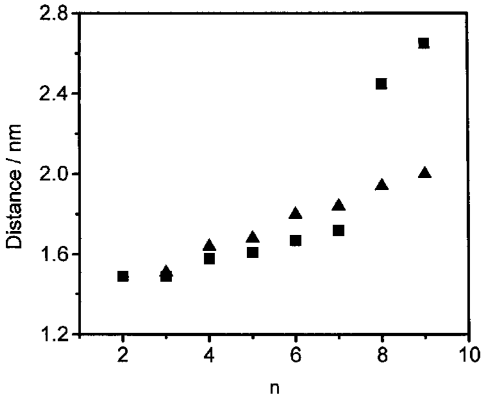


Figure 3. Distance between the columns in the columnar phase (▲) and lattice constants of the solid state at $T = 25°C$ (■), obtained from X-ray diffraction. The intercolumnar distances (▲) were measured at any of the temperatures 80, 120, 160 or 200°C which is in the respective temperature range of the columnar phase. Comparison of the respective distances measured at the different temperatures for the same compound reveals no significant temperature dependence.

For the $n = 2$–7 homologues, the solid lattice constant is very similar to the columnar spacing. This result seems to indicate that the columnar structure persists in the solid state. However, the solid phases occurring at room temperature for the $n = 8$ and 9 homologues show lattice constants that differ considerably from those of the columnar phase. This result is in agreement with our DSC measurements which indicate that these higher homologues show an additional solid–solid phase transition above room temperature. A closer investigation of this transition would require X-ray measurements on oriented samples for which further work is needed.

The chloroform solutions of all compounds show a bright green–yellow fluorescence, even under daylight conditions. The absorption and fluorescence spectra of the nonyl-ester in dilute solution are given in figure 4.

Both the absorption and fluorescence bands show a fine structure with two peaks and one shoulder. The positions of the respective peaks and the Stokes shift are summarized in table 2. The alkyl chain length has only

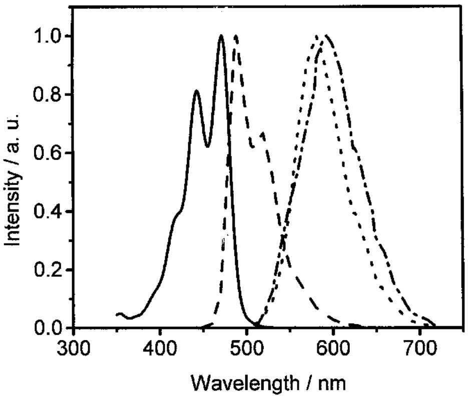


Figure 4. Absorption (—) and fluorescence spectra (– – –) of a dilute solution ($10^{-5}\,mol\,l^{-1}$) of the $n = 9$ homologue in chloroform, and of the pure compound in the (–·–·–·) columnar and (----) solid states.

Table 2. Wavelengths of maximum absorption and fluorescence for dilute solutions of the perylene dyes in chloroform.

	Absorption		Fluorescence		
n	λ_1/nm	λ_2/nm	λ_1/nm	λ_2/nm	Stokes shift $\Delta\lambda$/nm
2	443	472	487	519	15
3	443	472	490	520	18
4	444	472	491	521	19
5	443	472	491	520	19
6	444	472	490	520	18
7	444	472	490	519	18
8	444	472	490	520	18
9	444	472	489	520	17

a small influence on the wavelengths of absorption and fluorescence. This result is in agreement with earlier observations of similar materials [19].

In contrast to the dilute solutions (fluorescence peaks at 489 and 520 nm), crystals of the pure compounds show an orange fluorescence with one peak at 606 nm ($n=2$) to 582 nm ($n=9$) at room temperature. The colour shift by ≈ 80 nm between the fluorescence of the solutions and the pure compounds is remarkable. In addition, the spectra of the pure compounds show almost no vibrational structure. Both the colour shift and the loss of fine structure are typical for fluorescence resulting from excimers (photodimers). Excimers (= excited dimers) are formed if a monomer molecule is electronically excited due to absorption of a photon and reacts with an unexcited monomer. According to Stevens and Ban [20], the red-shift can be explained by two contributions (figure 5).

The energy level of the ground state of the two monomers increases with decreasing distance between the two monomer molecules. At the same time, the formation of an excited dimer from an excited and an unexcited monomer results in a decrease ΔH_A in the energy of the excited state. Both effects, the increase of the ground state energy by E_R and the decrease of the excited state energy by ΔH_A, cause a red shift of the fluorescence. Since excimers are only stable in the excited state, the absorption of light is always due to monomer molecules. Thus, the absorption spectra of the crystals have the same shape as the absorption spectra of the dilute solutions. The comparison of the absorption spectra (figure 6) reveals a slight bathochromic shift and a spectral broadening of the absorption in the crystalline state with respect to the dilute solution. However, there is no additional peak. Further information can be obtained from our dynamic measurements. The time dependence of the fluorescence intensity of the dilute solutions shows an exponential decay with a time constant of $\tau \approx 4.4$ ns. However, the fluorescence lifetime in the crystalline state and in the mesophase is much longer ($\tau \approx 16$ ns). This is an additional confirmation that the observed fluorescence results from excimers [21].

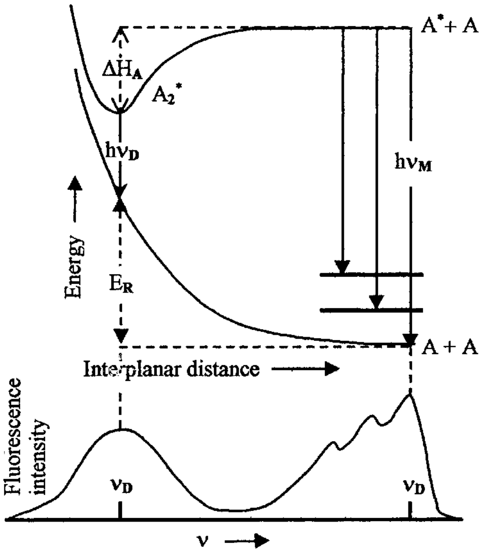


Figure 5. Energy levels of the monomer and excited dimer of a dye molecule, according to the theory of Stevens and Ban [20].

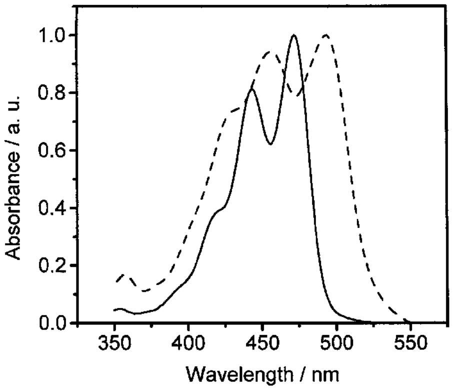


Figure 6. Comparison of the absorption spectra of (—) a dilute solution of the $n=9$ homologue in chloroform, and (----) the pure compound in the solid state.

Fluorescence of excimers is often observed in the solid state and in highly concentrated solutions of flat aromatic molecules; in mesophases of 4-alkyl-4′-cyano-biphenyls [22] and discotic liquid crystals, fluorescence resulting from excimers has been noticed as well. Figure 4 shows that there is a small difference between the fluorescence bands of the solid and the liquid crystalline states. The fluorescence peak appearing in the mesophase is slightly red-shifted compared to that of the solid state. A similar effect has also been observed in calamitic liquid crystals [22]. We speculate that there is a larger overlap between the molecules in the columnar hexagonal phase which leads to this red shift. (As the distance between molecules is less well defined in the liquid crystalline state, some molecules may temporarily be closer to each other than in the crystalline solid, thus offering low energy emission sites that may dominate the spectrum even if *on average* the molecules are not closer to their neighbours than in the solid.) In a similar manner, the slight increase in the fluorescence wavelength with decreasing chain length observed in our homologous series may be explained by an increasing overlap of the molecules. If the perylene derivatives are heated to the isotropic state, the fluorescence maxima are blue-shifted with respect to the columnar hexagonal phase. We suppose that the thermal expansion reduces the overlap between the molecules. A larger distance should lead to a decrease in the wavelength according to the energy level diagram by Stevens and Ban [20]. A red shift of the fluorescence with increasing dye concentration has also been demonstrated for a non-mesogenic system consisting of fluorescent coronene derivatives embedded in a polystyrene matrix [23]. The latter system shows a red shift of the fluorescence maxima with increasing dye concentration which was attributed to the increasing number of molecules which are accumulated within a microdomain.

The intensity of fluorescence decreases with increasing temperature (figure 7). It is interesting to note that this decrease in intensity is not continuous, but shows distinct steps at the phase transition temperatures. Figure 7 shows a comparison between the temperature dependence of the fluorescence intensity and DSC measurements.

The temperatures where the entropy changes discontinuously agree very well with the temperatures where the fluorescence intensity shows a discontinuity. This agreement is also shown in figure 2 for the different homologues. The decrease of the fluorescence intensity with increasing temperature may be explained by the increasing probability of non-radiative deactivation processes. The melting transition is much more easily detectable than the clearing transition from the fluorescence data. Although measuring the temperature dependence of the fluorescence intensity cannot replace DSC studies, it may be a useful complement [24].

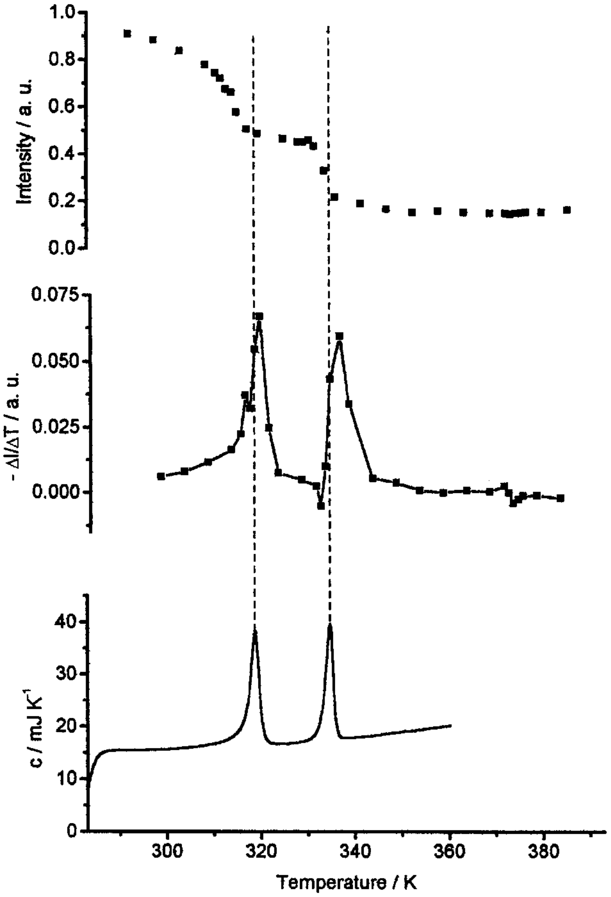


Figure 7. Temperature dependence of the fluorescence intensity (top), the heat capacity (DSC trace, bottom), and the absolute value of the temperature coefficient of the fluorescence intensity (centre) for the $n = 9$ homologue.

The results described so far were obtained for samples with homeotropic orientation. However, a uniform planar orientation of the columns could also be achieved. For the latter purpose, the liquid crystal was sandwiched between two quartz plates and heated to the temperature range of the columnar mesophase. Subsequent shearing of the two glass plates causes a unidirectional flow of the liquid crystal which in turn results in a highly birefringent sample. We conclude that the columns are uniaxially oriented parallel to the quartz plates. This is confirmed by measurements of the fluorescence dichroism (figure 8). When samples with this parallel alignment are illuminated with unpolarized light, the fluorescence light shows a preferred plane of polarization which can be detected by the intensity variation due to rotation of a linear analyser. It is interesting to note that the dichroism persists even in the solid phase when the sample is cooled below the melting point.

4. Conclusion

In summary, the homologous series of perylene derivatives investigated shows columnar phases over a broad temperature range. This columnar phase, i.e. a fluid state with orientational order, may be used to anneal the columnar structure in order to get an oriented thin film with a reduced number of defects. The X-ray data show that the columnar structure is also present in the solid state, at least for the lower homologues ($n \leqslant 7$). The fluorescence properties are similar to those of non-mesogenic PTCDA. The emission peak of the pure compounds is red-shifted compared with that for dilute

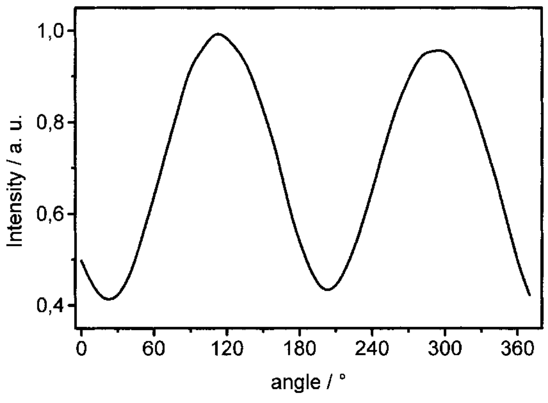


Figure 8. Dependence of the fluorescence intensity at $\lambda = 583$ nm on the azimuthal orientation of a linear analyser.

solutions, which indicates the formation of excimers. This is confirmed by the elongated fluorescence lifetimes. Dichroic fluorescent samples can be obtained by shearing these materials between the quartz substrates. This result may be useful in the search for polarized light emitting OLEDs. Promising first results concerning the electroluminescence of bilayer OLEDs based on one of these tetra-alkyl perylenetetracarboxylates are published elsewhere [18].

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