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Photophysical Properties of Discotic Dibenzopyrenes

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The photophysical properties of three discogenic dibenzopyrenes substituted by eight pentyloxy (O5DPB), heptyloxy (O7DBPP) or decyloxy (O10DBP) side chains are studied in solution and thin films. It is shown that the absorption and fluorescence spectra of the columnar mesophases are clearly distinguishable from those of the corresponding crystalline phases, allowing the study of phase transitions. Thus, it is found that the shorter the lateral chain length, the slower the crystallisation process. For O5DBP, the supercooled mesophase is stable over a period of at least one year; it crystallises after cooling below the glassy transition. Such a behaviour gives rise to temperature controlled optical bistability based on the position of the lowest energy absorption band and illustrated by a hysterisis loop.

Keywords: Columnar liquid crystals; bistability; optical properties; fluorescence; phase transitions

1. INTRODUCTION

The past few years we have been studying the photophysical properties of columnar liquid crystals [1–6]. In particular, we have been interested in the characterization of the excited states [3–6] and energy transfer [1, 2, 6] in these organized molecular systems. Within this context, we have investigated

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columnar mesophases formed by triphenylene [2, 3, 6], phthalocyanine [1] and triaryl pyrylium derivatives [4, 5].

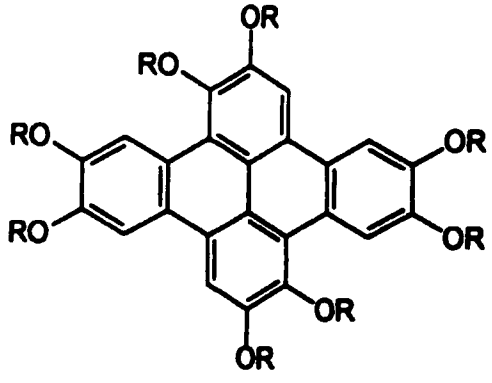
In the present communication, we focus our attention into another family of discogenic compounds the 1, 2, 5, 6, 8, 9, 12, 13-octakis(*n*-alkyloxy)dibenzopyrenes substituted by pentyloxy (O5DBP), heptyloxy (O7DBP) or decyloxy (O10DBP) side chains. All three compounds form hexagonal discotic columnar mesophases (D_h) [7, 8]. The phase transitions have been determined previously by means of polarizing microscopy and differential scanning calorimetry (DSC) and they are summarized on Table I. The heptyloxy and decyloxy derivatives exhibit a crystalline phase (K) at room temperature, the $K \rightarrow D_h$ transition occuring at 47 and 42°C respectively. In contrast, the D_h phase of O5DBP was found to be stable down to -35°C, temperature at which a glassy transition takes place.

The aim of our work is to determine the photophysical properties of those compounds in solution (§3) and neat thin films (§4) and to study the phase transitions with the help of absorption and fluorescence spectroscopy.

2. EXPERIMENTAL SECTION

The synthesis of the 1, 2, 5, 6, 8, 9, 12, 13-octakis(*n*-alkyloxy)dibenzopyrenes is described elsewhere [7, 8].

In order to record absorption spectra of thin films it was crucial to follow an appropriate cleaning procedure of the quartz slides used. They were sonicated successively in dichloromethane, detergent solution, distilled water



O5DBP, R=C_5H_{11}
O7DBP, R=C_7H_{15}
O10DBP, R=$C_{10}H_{21}$

FIGURE 1 Schematic representation of the studied 1, 2, 5, 6, 8, 9, 12, 13-octakis(*n*-alkyloxy) dibenzopyrenes.

TABLE I Phase transitions of 1,2,5,6,8,9,12,13-octakis (*n*-alkyloxy) dibenzopyrenes [7,8] K: crystalline phase, D_h: columnar hexagonal mesophase, I: isotropic phase

O5DBP	g(−35°C) D_h(96°C) I
O7DBP	K(47°C) D_h(107°C) I
O10DBP	K(42°C) D_h(105°C) I

and ethanol (20 min each time) and, then, pyrolyzed at 300°C. The spectroscopic cells were prepared by pressing together two slides and filled by capillary effect upon heating the powder compound to its isotropic phase. The sample alignment was checked by using polarizing microscope (Leitz equipped with a Mettler temperature controller). During the spectroscopic measurements the temperature of the thin films was regulated using an Oxford Instrument liquid nitrogen cryostat (DN1704) equipped with a PID temperature controller unit (ITC-4).

Absorption spectra were obtained on a Cary 3E spectrophotometer. Corrected steady state fluorescence spectra were recorded with SPEX Fluorolog-2. For the organized phases, the exciting beam was perpendicular to the surface of the cell and fluorescence was collected at an angle of 20° with respect to the incident beam. Polarized spectra were obtained by using HNP'P polaroid films. Quinine sulfate dihydrate in $HClO_4$ was used as a reference ($\phi_{fl} = 0.59$) [9] for fluorescence quantum yields. Fluorescence decays were recorded by the single photon-counting technique. The excitation source was the second harmonic of a rhodamine 6G dye laser and the detector a microchannel plate (R1564U Hamamatsu).

2. RESULTS AND DISCUSSION

Properties of Solutions

The absorption spectrum of O7DBP in dichloromethane (10^{-6}M), presented in Figure 2, is very structured. Three intense maxima at 231, 296 and 313 nm are observed. At lower energy, two intermediate (344 and 358 nm) and two low (375 and 398 nm) intensity bands are present. The fluorescence spectrum peaks at 402 nm. Four vibronic bands separated by 1270 cm^{-1} can be clearly seen. They are attributed to the aromatic C—H bending vibration [10]. The excitation spectrum overlaps the absorption one, showing that internal conversion from the upper excited singlet states to the lowest one proceeds with unit quantum efficiency. The Stokes shift deter-

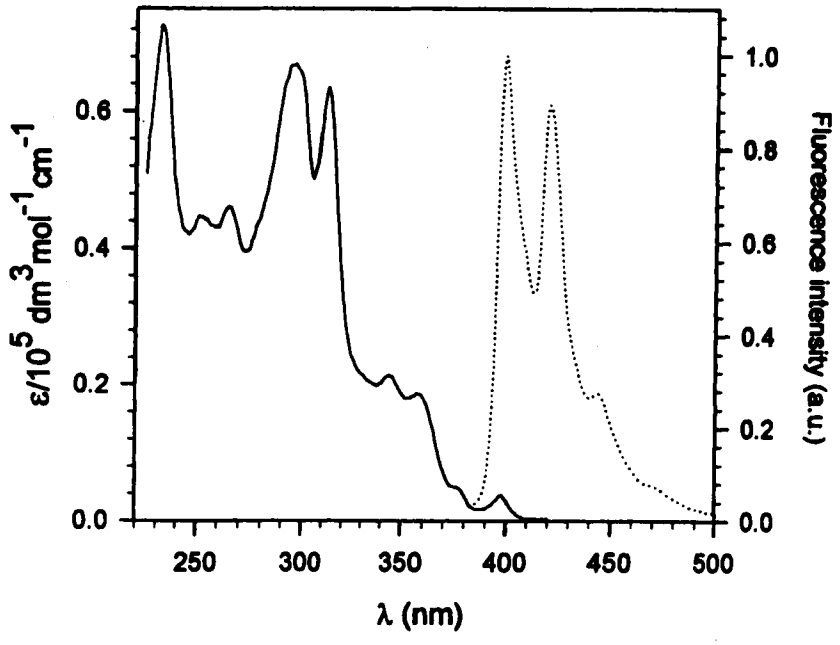


FIGURE 2 Absorption (——) and (-----) fluorescence spectra of O7DBP in dichloromethane; $\lambda_{ex} = 375$ nm.

mined as the energy difference between the fluorescence maximum and the maximum of the lowest energy absorption band is quite small, 300 cm^{-1}, indicating that the ground state and the fluorescent state have similar geometries. The solvent polarity has not an important influence on the spectra; in various solvents having dielectric constants between 1.9 and 48.9 the spectral shifts are smaller than 200 (absorption) and 400 cm^{-1} (fluorescence).

The fluorescence lifetime obtained for O7DBP toluene solutions can be fitted by a single exponential yielding a lifetime of 6.17 ns. The fluorescence quantum yield ϕ_f is 0.26. The radiative lifetime τ_{rad} of the emitting state, determined as τ_f/ϕ_f is 25 ns, corresponding to a moderately allowed transition.

All the above described photophysical properties of O5DBP and O10DBP in solution are the same as those of O7DBP, showing they are not affected by the lateral chain length. The same conclusion was drawn from the study of discotic triphenylenes substituted by six pentyloxy, heptyloxy or nonyloxy side chains [6].

Properties of Thin Films

The mesophase absorption and fluorescence spectra of three examined compounds are practically the same. The linearly polarized absorption spectra of aligned thin films did not reveal any dichroism. This means that the transition moments are randomly distributed within the plane of the electric light vector which is parallel to the surface of the films. Taking into account that the electronic transitions are polarized within the aromatic plane and that the aromatic planes are all parallel since the samples are aligned, we deduce that the central cores are parallel to the slides of the spectroscopic cell (homeotropic alignment).

The mesophases (Fig. 3) exhibit the same absorption bands as those observed for dichloromethane solutions (Fig. 2), although, in the former case, many of the peaks are less resolved. However, we can clearly see that the highest energy absorption peak (228 nm) in the mesophase spectrum is blue-shifted with respect to its position in the solution spectrum by *ca.* 570 cm^{-1}, while the lowest energy one (403 nm) is red-shifted by *ca.* 310 cm^{-1}. Hypsochromic shifts have been already reported for intense transi-

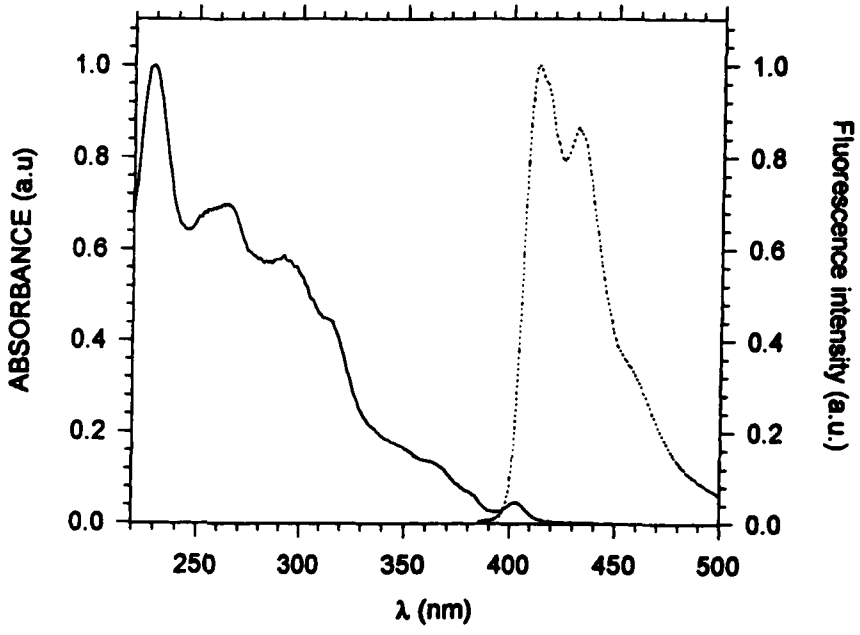


FIGURE 3 Absorption (——) and fluorescence (-----) spectra of the O7DBP mesophase obtained for aligned thin films at 55°C; $\lambda_{ex} = 356$ nm.

tions of other columnar phases [1, 5, 6] and were attributed to strong exciton coupling between the transition moments of the molecules stacked in the same column [4, 6]. In contrast, the bathochromic shift cannot be correlated to the formation of exciton states, as in the case of J aggregates. Indeed, such a shift is observed when the stacking axis forms with the normal to the molecular planes an angle larger than the magic angle [11]. This condition is not fulfilled for the examined phases characterized by a hexagonal lattice. Moreover, the red-shift is observed for a moderately allowed transition for which the exciton coupling is expected to be relatively weak compared to thermal fluctuations. Therefore, it could be related to different conformations of the side chains near the aromatic core in solution and in the mesophase. As a matter of fact, such conformational changes may influence the energy of electronic transitions [12].

The fluorescence spectra of the mesophases (Fig. 3), peaking at 413 nm, have a profile similar to that observed for solutions. The vibronic structure is still present although the energy difference between the vibronic repliqua has decreased (1000 cm^{-1} instead of 1270 cm^{-1}). Moreover, the Stokes shift has increased by at least a factor of two, indicating that relaxation in the lower excited state is more important in the mesophase than in solution. This latter finding seems to be contrary to intuition, since the degrees of freedom are expected to be greater in solution. This could suggest that relaxation in the organized system involves cooperative effects.

The absorption and fluorescence spectra of the O7DBP crystalline phase are practically the same as those of the O10DBP crystalline phase. They are clearly distinguishable from the mesophase spectra. Figure 4a shows the absorption spectra of a O7DBP thin film, recorded at room temperature as a function of time, after heating till the temperature domain of the mesophase. The initial spectrum is that of the mesophase which is supercooled at room temperature. Progressively, crystallisation takes place and is accompanied by a change in the spectrum profile. We have observed in the polarizing microscope that crystallization of those films is accompanied by a loss of the macroscopic alignment of the sample.

It can be seen in Figure 4a that, upon crystallization, the intensity of the high energy absorption bands decreases. This happens because the transition dipoles, initially randomly distributed within the plane of the light electric field vector, orientate in a different way. Further changes appear in the low energy region of the spectrum, corresponding to rather weak electronic transitions: the intensity of the peaks at 350 and 365 nm increases and their relative importance is inverted while the lowest energy band is blue-shifted and becomes narrower. This behavior could be due, besides the

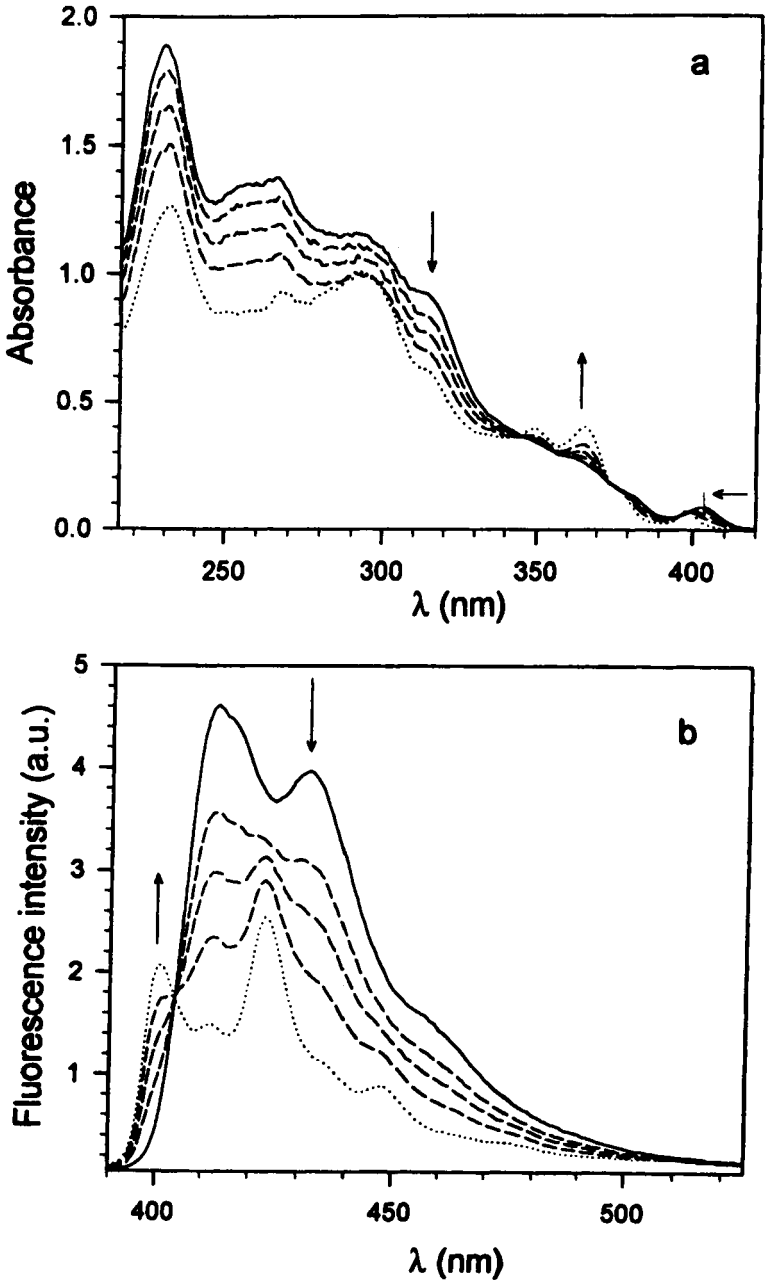


FIGURE 4 Changes in absorption (**a**) and fluorescence (**b**) spectra of a O7DBP thin film observed during the crystallization process. The sample is heated to 55°C (D_h) and then rapidly cooled to 20°C. The spectra are recorded at 40 mn intervals; $\lambda_{ex} = 375$ nm. The initial (——) and final (·····) spectra correspond to D_h and crystalline phases, respectively.

loss of the macroscopic sample alignment, to the conformational changes mentioned above.

The crystallisation process can also be followed through the changes in fluorescence spectra. During the $D_h \rightarrow K$ transition, the fluorescence spectrum is hypsochromically shifted, decreases in intensity and becomes more structured. Upon excitation at the isosbestic points, an isoemissive point is observed (Fig. 4b).

By recording absorption and fluorescence spectra as a function of time, we have found that crystallisation at room temperature is more rapid for O10DBP than for O7DBP. For the former it occurs within a few minutes, while a few hours are required for the latter.

At this point we conclude that it is possible to follow the phase transitions $D_h \leftrightarrow K$ using optical spectroscopy. In the continuation of the present work, we will investigate in this way the thermal behaviour of O5DBP, reported [7, 8] to be different than that of O7DBP and O10DBP (Tab. I).

Based on spectroscopic measurements, we found that the O5DBP mesophase is stable at room temperature, at least over a period of one year, in agreement with the X-ray diffraction and DSC experiments. Upon cooling below the glassy transition, no change is observed in the absorption spectra showing that the Franck-Condon transitions have practically the same properties in the liquid crystalline and the glassy state. Under the same conditions, the fluorescence intensity increases (Fig. 5, black circles) because the non radiative deactivation rate constant decreases. If the sample is kept at $-33°C$ for a few minutes only and then heated again to room temperature, reversible fluorescence changes are observed (Fig. 5, white circles). If the sample remains at $-33°C$ for a longer time (typically one-two days), both the absorption and fluorescence spectra do not correspond any more to the mesophase ones but they become similar to those obtained for the O7DBP and O10DBP crystalline phases, indicating that crystallisation takes place. The DSC measurements which revealed the formation of a glassy state at $-35°C$ but not of a crystalline one [7, 8] were performed at a relatively high speed (10°C/min). This is not surprising, because, according to our experiments, the crystallisation process of O5DBP is very slow. The O5DBP crystalline phase formed in that way is stable up to 40°C, temperature at which it starts to be transformed to the mesophase. We have also found that the fluorescence spectrum of the O5DBP powder compound obtained through crystallisation from a solvent corresponds to the spectrum of the crystalline phase and not to that of the mesophase.

The thermal behaviour of O5DPB thin films can be illustrated by plotting the film absorbance at 403 nm (A_{403}) as a function of temperature (Fig. 6).

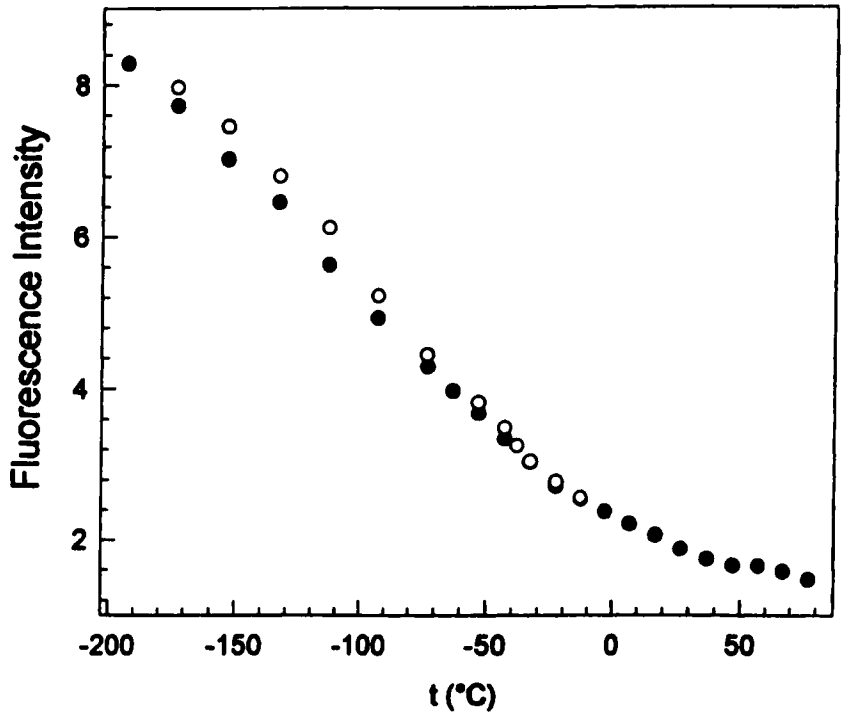


FIGURE 5 Variation of the normalized total fluorescence intensity of O5DBP thin films determined starting from the mesophase upon cooling (black circles) and then heating (white circles). time interval between two successive measurements: 6 mn; $\lambda_{ex} = 356$ nm.

The A_{403} of a crystalline film has a constant value (typically 0.1 for a thickness of 5μ) between -60°C and 40°C. Then it increases abruptly by one order of magnitude. The new value is constant between 80°C and -10°C. Thus the variation of A_{403} recorded during a heating and cooling cycle forms a hysterisis loop, corresponding to a thermally controlled optical bistability.

Our spectroscopic results concerning the thermal behaviour of O5DBP are also confirmed by polarizing microscopy. The crystalline phase formed at low temperature is transformed to the mesophase at *ca.* 46°C. This temperature is quite close to those corresponding to the phase transitions of O7DBP and O10DBP (Tab. I). The fact that crystallisation occurs at low temperature suggests that the primary nucleation processes are faster near the glassy state. The nucleation sites created in this way lead to the formation of the crystalline phase thermodynamically stable at room temperature. Finally, it is worth-noticing that lack of crystallization at room temperature

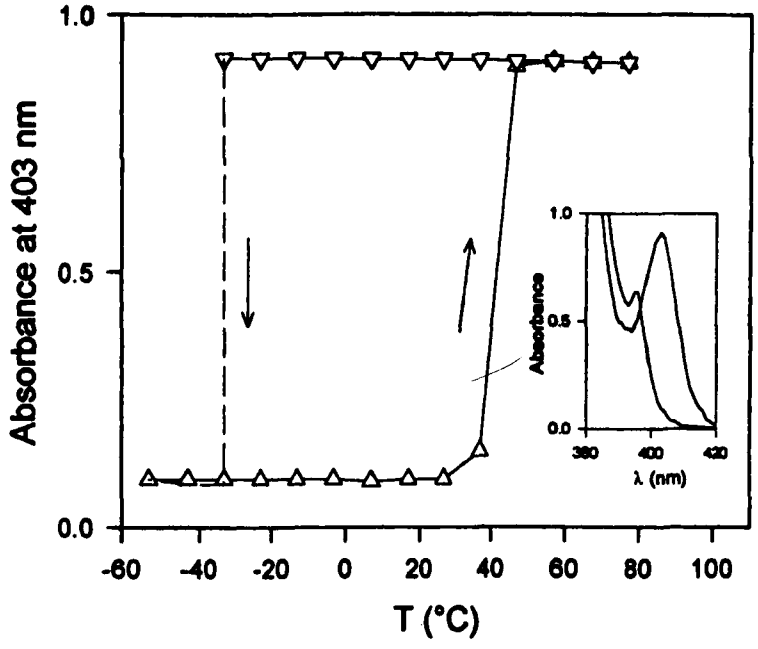


FIGURE 6 Absorbance changes observed at 403 nm for a thin film of O5DBP during a heating and cooling cycle (1°C/min). The dashed line corresponds to a waiting time of two days.

is also reported for a ferroelectric columnar mesophase formed by a chiral dibenzopyrene derivative [13].

4. SUMMARY AND CONCLUSIONS

The main findings of the present work dealing with discotic octa-alkyloxy dibenzopyrenes can be summarized as follows.

Solutions of the examined compounds in various solvents show fluorescence peaking at 400 ± 2 nm. The fluorescence lifetime is 6.17 ns and the fluorescence quantum yield 0.26.

The side chain length does not have any influence on the absorption and fluorescence spectra of both solutions and thin films. Conversely, the profile of these spectra greatly depends on the molecular arrangement.

We have shown that phase transitions can be detected by absorption and fluorescence spectroscopy. It has been found that the shorter the side chains the slower the crystallisation. The O5DBP mesophase, supercooled at room

temperature, is stable for at least one year. It can crystallize after cooling down to the glassy state. The crystalline phase is stable up to 40–46°C. The thermal behaviour of O5DPB thin films can be followed through the change of the lowest absorption band. The mesophase absorbance at 403 nm being by an order of magnitude higher than that of the crystalline one, O5DBP films present, for a period of at least one year, a thermally controlled optical bistability illustrated by a hysterisis loop.

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References

[1] D. Markovitsi, I. Lécuyer and J. Simon, *J. Phys. Chem.*, **95**, 3620 (1991).
[2] D. Markovitsi, I. Lécuyer, P. Lianos and J. Malthête, *J. Chem. Soc. Faraday Trans.*, **87**, 1785 (1991).
[3] D. Markovitsi, H. Bengs and H. Ringsdorf, *J. Chem. Soc. Faraday Trans.*, **88**, 1275 (1992).
[4] C. Ecoffet, D. Markovitsi, P. Millié and J. P. Lemaistre, *Chem. Phys.*, **177**, 629 (1993).
[5] C. Ecoffet, D. Markovitsi, C. Jallabert, H. Strzelecka and M. Veber, *Thin solid films*, **242**, 83 (1994).
[6] D. Markovitsi, A. Germain, P. Millié, P. Lecuyer, L. Gallos, P. Argyrakis, H. Bengs and H. Ringsdorf, *J. Phys. Chem.*, **99**, 1005 (1995).
[7] P. Henderson, H. Ringsdorf and P. Schuhmacher, *Liq. Crystals*, **18**, 191 (1995).
[8] P. Schuhmacher, Doctoral Dissertation; University of Mainz, 1995.
[9] R. A. Velapoldi and K. D. Mielenz, *NBS Spec. Publ.*, 260 (1980).
[10] G. Kruk, A. Kocot, R. Wrzalik, J. K. Vij, O. Karthaus and H. Ringsdorf, *Liq. Cryst.*, **14**, 807 (1993).
[11] M. Kasha, H. R. Rawls and M. Ashraf El-Bayoumi, *Pure Appl. Chem.*, **11**, 371 (1965).
[12] A. Zehnacker, F. Lahmani, E. Bréhéret, J. P. Desvergne, H. Bouas-Laurent, A. Germain, V. Brenner and P. Millié, *Chem. Phys.*, **208**, 243 (1996).
[13] H. Bock and Helfrich, *Liq. Crystals*, **18**, 387 (1995).