

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Photophysical properties of discogenic triaryl pyrylium salts Excimer migration in columnar liquid crystals

D. Markovitsi^a; I. Lécuyer^a; B. Clergeot^a; C. Jallabert^b; H. Strzelecka^b; M. Veber^b

^a Ua Cea-Cnrs 331, Cen/Saclay Irdi/Desicp/Dlpc/Scm, Gif sur Yvette, Cedex, France ^b Espci, Paris, Cedex 05, France

To cite this Article Markovitsi, D. , Lécuyer, I. , Clergeot, B. , Jallabert, C. , Strzelecka, H. and Veber, M.(1989) 'Photophysical properties of discogenic triaryl pyrylium salts Excimer migration in columnar liquid crystals', *Liquid Crystals*, 6: 1, 83 – 92

To link to this Article: DOI: 10.1080/02678298908027325

URL: <http://dx.doi.org/10.1080/02678298908027325>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photophysical properties of discogenic triaryl pyrylium salts Excimer migration in columnar liquid crystals

by D. MARKOVITSI, I. LÉCUYER and B. CLERGEOT
CEN/SACLAY IRDI/DESICP/DLPC/SCM, UA CEA-CNRS 331,
91191 Gif sur Yvette Cedex, France

C. JALLABERT, H. STRZELECKA and M. VEBER
ESPCI, UA 429, 10, rue Vauquelin, 75231 Paris Cedex 05, France

(Received 11 October 1988; accepted 24 February 1989)

The photophysical properties of a homologous series of 2,4,6-triaryl pyrylium tetrafluoroborates substituted by six alkoxy chains ($C_nH_{2n+1}O$, $n = 2, 3, 4, 5, 8, 12$) are reported. In dilute solution, the electronic absorption and fluorescence spectra do not depend on the length of the alkoxy chains while both fluorescence lifetimes and fluorescence quantum yields increase when the chain length increases. Monomer and excimer fluorescence is observed with the pure compounds; the steady state and time resolved emission spectra and the decay kinetics which do not depend on the chain length suggest that the columnar structure exist with very short lateral chains. Excimer lifetimes determined in the liquid-crystalline phases follow an exponential law as a function of the reciprocal temperature: $\tau \propto \exp(E_M/RT)$. The activation energy for excimer migration is 0.046 eV, 0.061 eV and 0.087 eV respectively for $n = 5, 8$ and 12.

1. Introduction

We have started recently a systematic study of the photophysical properties of columnar liquid crystals in order to characterize these materials better [1-3]. Such mesophases can consist of disc-like molecules containing a flat and rigid core surrounded by flexible chains [4, 5]. Their structure corresponds to stacks of molecular discs forming segregated columns; the intercolumnar distance is much larger than the intermolecular distance within the columns. These geometrical features make the columnar phases interesting systems for the study of one dimensional energy migration. In this context, the luminescence properties of an hexa-substituted triphenylene has been published [1]. Laser-induced triplet excitons have been also described for metal free and zinc octasubstituted phthalocyanines [2, 3].

The present paper is concerned with an homologous series of ionic discogenic compounds, the 2,4,6-triaryl pyrylium fluoroborates (C_nPy , see figure 1) substituted by six alkoxy chains ($C_nH_{2n+1}O$, $n = 2, 3, 4, 5, 8, 12$). It is well-established that for $n = 5, 8, 12$ the C_nPY salts exhibit columnar mesophases from room temperature to 200-250°C. For $n = 4$ a crystalline to liquid-crystalline transition is observed at about 100°C. X-ray diffraction experiments are consistent with an ordered hexagonal columnar phase (D_{ho}) [6-8]. The structural characteristics of the C_2Py and C_3Py are not known.

The photophysical properties described here have been studied with both dilute homogeneous solutions and with non-oriented columnar phases of the pure compounds (thin films).

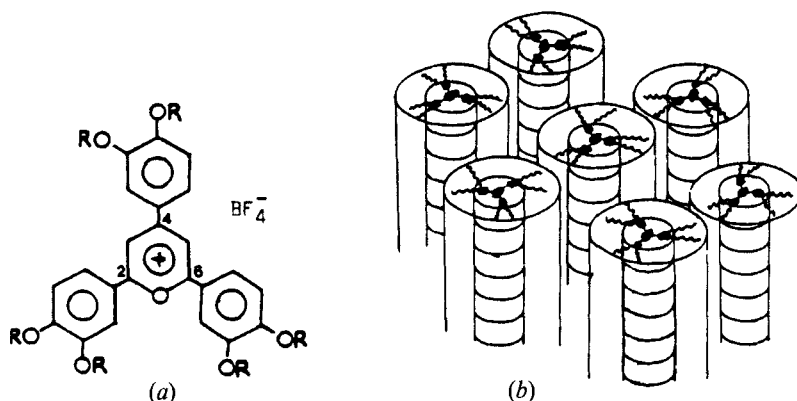


Figure 1. Schematic representation of (a) 2,4,6-triarylpyrylium tetrafluoroborates (C_n Py) $R = C_nH_{2n+1}$ with $n = 2,3,4,5,8$ or 12 , and (b) their columnar phases.

2. Experimental

The synthesis of the C_n Py salts is described in detail elsewhere [6–8]. Dichloromethane was spectroscopic grade (Fluka). The spectroscopic cells containing the pure compounds were prepared as follows: a few milligrams of the compound were deposited on a quartz slide which was heated at about 120°C and stuck on the surface of a quartz flow cell. Temperature control was achieved with water circulation in the flow cell using a HAAKE FE2 circulator. Steady state absorption spectra were recorded with a Beckman spectrophotometer (U.V. 5240). An LS5 Perkin–Elmer spectrofluorimeter was used for recording steady state luminescence spectra. Both steady state and time resolved luminescence experiments of pure compounds were performed with front face excitation.

Luminescence lifetimes and time resolved emission spectra were obtained using the single photon counting technique [9, 10]. The experimental set-up is shown in figure 2. The laser source consisted of a cavity dumped, mode locked dye laser

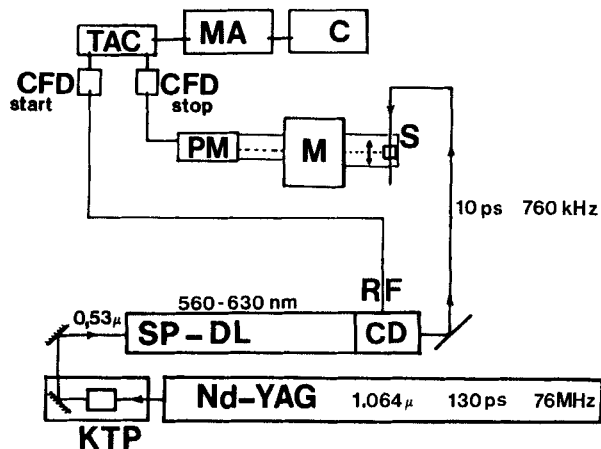


Figure 2. Experimental set-up: Nd-YAG, continuous wave, mode locked Nd-YAG laser; KTP, frequency doubling crystal; SP-DL, synchronously pumped dye laser; CD, cavity dumper; RF, radiofrequency signal; S, sample; M, monochromator; PM, photomultiplier; CFD, constant fraction discriminator; TAC, time to amplitude converter; MA, multichannel analyser; C, computer.

(Coherent, Model 701-3) synchronously pumped by the second harmonic 532 nm, 76 MHz, 1 W) of an actively mode locked Nd-YAG laser (Quantronix, Model 416). The dye laser repetition rate was reduced to 760 kHz and the pulse duration was 10 ps (fwhm) as measured using non-colinear autocorrelation. The average power at 580 nm was 30 mW. The start signal was given by the radio frequency signal of the cavity dumper and the luminescence emitted by the sample (stop signal) was detected by an uncooled red sensitive RTC 2254B photomultiplier. The start and stop signals were fed to an ORTEC 567 time to amplitude converter via two ORTEC 584 constant fraction discriminators. The output signals were processed in an ORTEC 7450 multichannel analyser (MCA) of 4096 channels, interfaced to a DEC PDP 11/73 computer. Both spectrometer and software for the decay curve analysis were provided by Edinburgh Instruments LTD.

The response functions needed for the reconvolutions were recorded using either the fluorescence of pinacyanol methanolic solution (lifetime: 7.6 ps [11] at the same wavelength as the luminescence of the solution studied or, in the case of a front face excitation, the scattered light on the sample surface. The decay curve analysis was performed by reconvolution of a theoretical decay (mono- or multi-exponential) with the instrumental profile. The experimental decay curve was then fitted using a least-squares fit. Statistical criteria systematically used are the normalized χ_r^2 and the residuals. In some cases the quality of the fit was also tested with the Durbin-Watson parameter and the autocorrelation function.

For the study of the columnar phases fluorescence decays, a Glan-Thompson calcite prism forming an angle of 54.7° with the laser polarization direction was positioned before the monochromator in order to avoid polarization artefacts. Before each experiment the apparatus was tested by measuring the fluorescence lifetime of undegassed rhodamine B in methanolic solution, τ was found to be (2.40 ± 0.02) ns, which is close to the accepted literature value [12].

3. Results and discussion

(a) Solutions

The absorption spectra obtained with the C_n Py salts in dichloromethane solution are identical for all the chain lengths and they are characterized by two bands in the near U.V.-visible region, peaking at 326 nm and 485 nm (see figure 3). The comparison

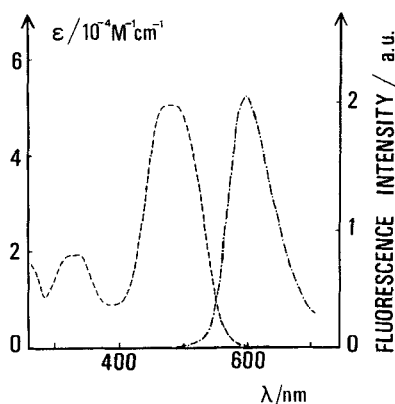


Figure 3. Steady state absorption (---) and luminescence (—) spectra of C_{12} Py; 10^{-6} M in CH_2Cl_2 , $\lambda_{ex} = 470$ nm.

Table 1. C_n Py fluorescence lifetimes and relative quantum yields; 10^{-7} M in dichloromethane, $\lambda_{\text{ex}} = 580$ nm.

n	τ_F/ns	ϕ_F
2	1.14	0.72
3	1.21	0.75
4	1.27	0.80
5	1.32	0.83
8	1.35	0.92
12	1.44	1.00

of these maxima with those obtained for other 2,6-diaryl and 2,4,6-triaryl pyrylium salts shows that these bands are due to $\pi \rightarrow \pi^*$ transitions polarized along the xx' axis of the pyrylium ion [8, 13, 14]. Moreover, the observed bands are red shifted with respect to those of the 2,4,6 triphenyl pyrylium salts (284 nm and 418 nm) because of charge delocalization involving the alkoxy groups.

It has been verified that the Beer-Lambert law is obeyed from 10^{-6} M to 5×10^{-4} M which means that no aggregation occurs in this concentration range.

The C_n Py fluorescence peaks at 587 nm and the excitation spectra are very close to the absorption ones. The value of the Stokes shift, 3600 cm^{-1} , is of the same order of magnitude as the shifts observed with other substituted pyrylium salts without long chains [15]. When the fluorescence decay curves are fitted with one exponential the χ_r^2 value is about 1.5. A fit with two exponentials is necessary to obtain an acceptable χ_r^2 (≤ 1.20); the first lifetime is then identical to that given by the one exponential fit (see table 1) while the second one has a very weak contribution to the total luminescence (< 5 per cent) and is hardly reproducible. Two luminescence lifetimes are reported for some pyrylium salts in homogeneous solutions and they are assigned to two different conformers [16, 17]. We think that the number of conformers should be much higher but there is one rotational position which is predominant and has a higher fluorescence quantum yield than the others.

The trend of the fluorescence lifetimes and quantum yields to increase with the chain length is evident from table 1. It is well established that when the rotation of the aryl groups is inhibited both the fluorescence lifetimes and quantum yields of the pyrylium salts increase [17]. We could correlate the trend observed here to a tendency of the alkyl chains to inhibit the rotation of the aryl substituents: in this way, the longer the chain length the more difficult the rotation and hence the greater the values of the fluorescence lifetimes and quantum yields. Moreover, the C_n Py salts fluorescence lifetimes are shorter than those observed for the other pyrylium derivatives. For example the 2,4,6-triphenyl pyrylium perchlorate has a fluorescence lifetime of 4.2 ns [15]. This phenomenon is due to the substitution of the phenyls with alkoxy groups which are known to reduce the fluorescence lifetimes of aromatic compounds [1, 18].

(b) Thin films

The absorption spectrum obtained with a C_{12} Py thin film at room temperature (see figure 4) consists of two very broad bands which cover the whole visible region; both bands are split and we can distinguish four peaks (325 nm, 360 nm, 478 nm, 576 nm). A similar broadening and splitting in the liquid crystal absorption spectrum with respect to that of the dilute solutions is also reported for the octasubstituted

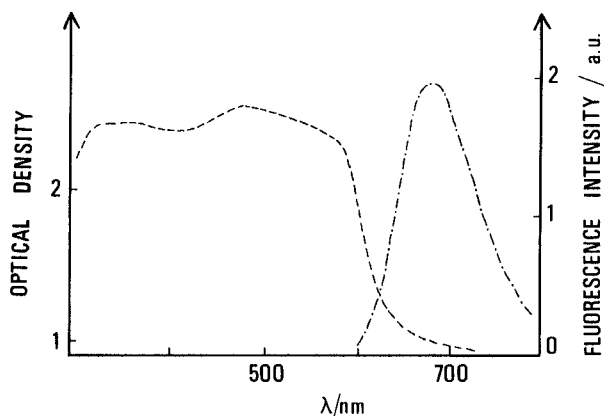


Figure 4. Steady state absorption (---) and luminescence (—) spectra of pure $C_{12}Py$; $20^{\circ}C$, $\lambda_{ex} = 480$ nm.

phthalocyanines; it is due to very strong intermolecular interactions in the mesophase [3]. The optical density of all the peaks is approximately the same, while in solution the higher energy maximum is 2.5 times smaller than the low energy one. Rayleigh scattering from the molecular aggregates, more intense at short wavelengths, is probably responsible for this phenomenon [19] which is observed with other columnar phases [20]. With increasing temperature up to $90^{\circ}C$ the spectral profile remains unchanged indicating that no significant modification of the ground state intermolecular interaction takes place in this temperature domain. The same absorption spectra are obtained with the C_8Py and C_5Py . In contrast, it was not possible to record the absorption spectra of C_2Py , C_3Py and C_4Py since these compounds are not liquid crystals at room temperature.

The luminescence spectra recorded with all of the C_nPy salts are identical. They have a peak at 685 nm, independent of the excitation wavelength. The plot of the $C_{12}Py$ luminescence intensity as a function of temperature shows a discontinuity at about $50^{\circ}C$ (see figure 5). The same discontinuity is observed in the temperature variation of the intercolumnar separation. Indeed, the change of the intercolumnar separation can induce a change in the material refractive index which has an effect on the luminescence intensity [21].

The luminescence decay curves obtained at a fixed emission wavelength do not depend on the laser wavelength in the range 557 nm–630 nm. This observation and the fact that the steady state luminescence spectrum does not vary with the excitation wavelength prove that the emitting species have the same ground state. In contrast the decay profile depends on the emission wavelength; the shorter the wavelength the more rapid the luminescence decay (see figure 6). A sum of three exponentials is necessary in order to fit the decay curve over the whole time range but the three lifetimes determined are different for each luminescence wavelength; they should not therefore have any physical meaning. In the first 750 ps after the peak count are neglected then the decay curves obtained at different emission wavelengths can be fitted to a sum of two exponentials using global analysis. Here

$$I(t) = C + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),$$

where C is a constant, A_1 , A_2 are pre-exponential factors, and τ_1 , τ_2 are luminescence lifetimes. According to this method, several decay curves are analysed simultaneously

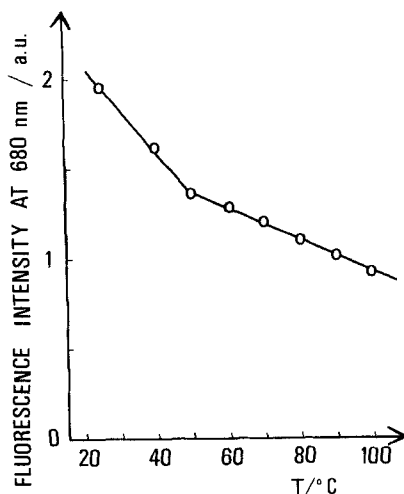


Figure 5. Temperature variations of the luminescence intensity obtained with pure $C_{12}Py$; $\lambda_{ex} = 480$ nm, $\lambda_{em} = 680$ nm.

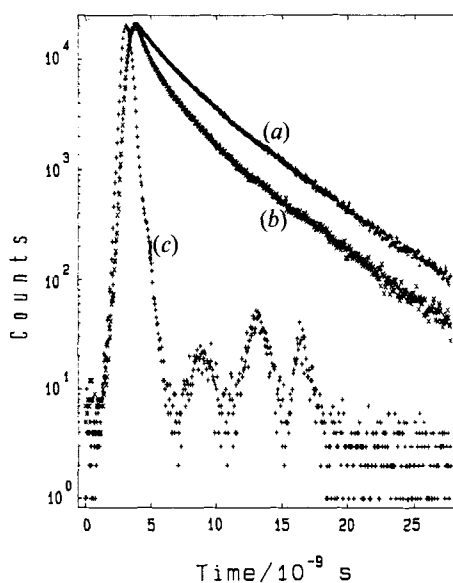


Figure 6. Decay curves obtained with the $C_{12}Py$ columnar phase at $20^\circ C$ (a) $\lambda_{em} = 750$ nm, (b) $\lambda_{em} = 630$ nm, (c) instrumental profile; $\lambda_{ex} = 580$ nm.

and the luminescence lifetimes τ_1 and τ_2 have the same value for all the wavelengths studied. Table 2 shows the τ_1 and τ_2 values as a function of the chain length. The contribution of τ_1 to the luminescence for the time domain analyzed is given by its relative amplitude: $\tau_1 A_1 / (\tau_1 A_1 + \tau_2 A_2)$. For all of the $C_n Py$ thin films the short lifetime relative amplitude decreases when the luminescence wavelength increases (see figure 7). This result is corroborated by the time resolved emission spectra obtained with time windows 0–100 ps and 10–20 ns: the first, where both luminescent species are present, is blue-shifted ($\lambda_{max} = 660$ nm) with respect to the second ($\lambda_{max} = 700$ nm)

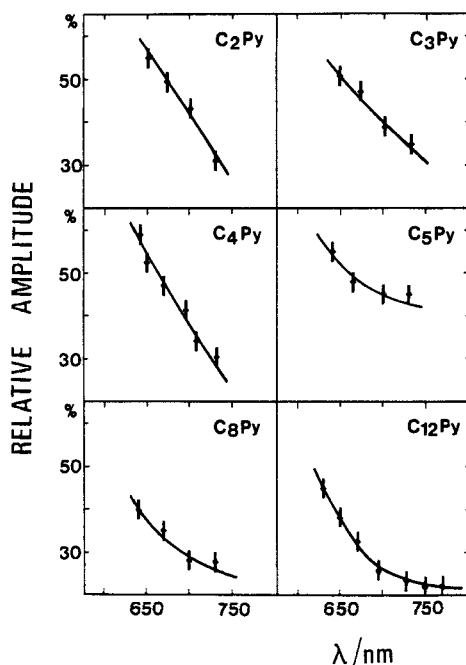


Figure 7. Luminescence relative amplitude of the short decay time ($\tau_1 = 1.6$ ns) for C_n Py thin films versus emission wavelength; 20°C , $\lambda_{\text{ex}} = 580$ nm.

Table 2. C_n Py thin film luminescence lifetimes; 20°C , $\lambda_{\text{ex}} = 580$ nm.

n	τ_1/ns	τ_2/ns
2	1.5 ± 0.2	3.9 ± 0.2
3	1.7 ± 0.2	4.2 ± 0.2
4	1.4 ± 0.2	4.2 ± 0.2
5	1.2 ± 0.2	4.0 ± 0.2
8	1.5 ± 0.2	4.3 ± 0.2
12	1.6 ± 0.2	4.3 ± 0.2

which corresponds exclusively to the long lived species (see figure 8). Outgassing the C_n Py columnar phases results in only a slight increase (≈ 20 per cent) of both τ_1 and τ_2 . This allows us to rule out the hypothesis that τ_2 corresponds to a phosphorescence lifetime quenched by oxygen [16].

Given that the two luminescent components have the same ground state, we assign the lifetime τ_1 to a monomer emission and the τ_2 to an excimer emission. This is in agreement with the fact that excimers have, in general, a lower energy and a longer lifetime than the corresponding monomers [22, 23]. The steady state and time-resolved fluorescence spectra compared to those obtained in dilute solutions indicate that the excimer emission is predominant. An additional proof for this statement comes from the temperature variation of the square of the fluorescence spectral width (fwhm); a linear relationship is observed, characteristic of the structureless gaussian-like excimer emission band [23]. Moreover, the fluorescence maximum of the C_n Py columnar phases shifts towards lower wavelengths with increasing temperature ($\lambda_{\text{max}} = 673$ nm at 150°C). Such a shift is also a general property of the

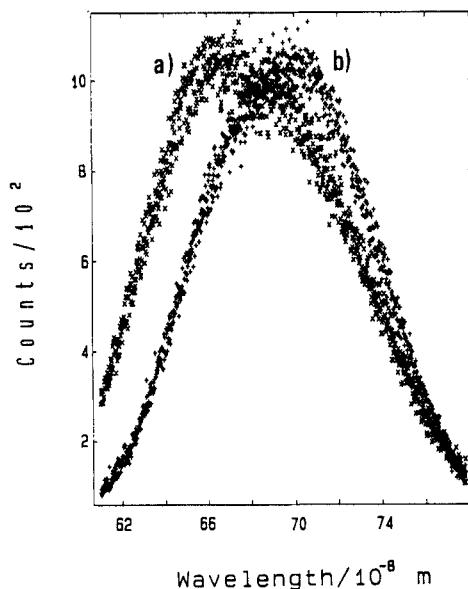
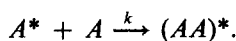


Figure 8. Time resolved emission spectra obtained with the $C_{12}Py$ columnar phase; time windows: (a) 0–100 ps, (b) 10–20 ns, $\lambda_{ex} = 580$ nm, $20^\circ C$.

excimers formed in a stack of molecules [23]. However, the decay curves recorded at different emission wavelengths do not show any rise time indicating excimer formation [9]. This is not surprising because excimer formation in the columnar phases corresponds to an oriented bimolecular reaction



The chromophores, A , consist of the aromatic parts of the discogenic compounds C_nPy which are all parallel with an interplanar distance of 3.4 \AA [6–8]. For pyrene single crystals where the interplanar distance is also 3.4 \AA , it has been demonstrated, by time resolved absorption spectroscopy, that the excimer formation time, $\tau = 1/k$, is 140 fs at room temperature [24]. This time is shorter than the resolution of our experiment set-up (55 ps).

The initial non-exponential part of the decay is attributed to energy migration [25]. In molecular crystals both monomer and excimer excitation may be delocalized and both of them act as energy traps [23, 26, 27]. In columnar liquid crystals traps can be easily formed when the discontinuity of the columns breaks down locally [28]. In this way the column length should determine the exciton path-length and therefore the number of hops of the excitation energy from one molecule to the other. The number of hops is described by [26]

$$n = \tau/\tau_h,$$

where τ is the exciton lifetime and τ_h is the hopping time. The hopping time follows, with the reciprocal of the temperature, an exponential law

$$\tau_h = \tau_h^0 \exp(E_M/RT)$$

where E_M is the activation energy for the exciton migration. For the columnar phases n is constant (determined by the column length) and the exciton lifetime

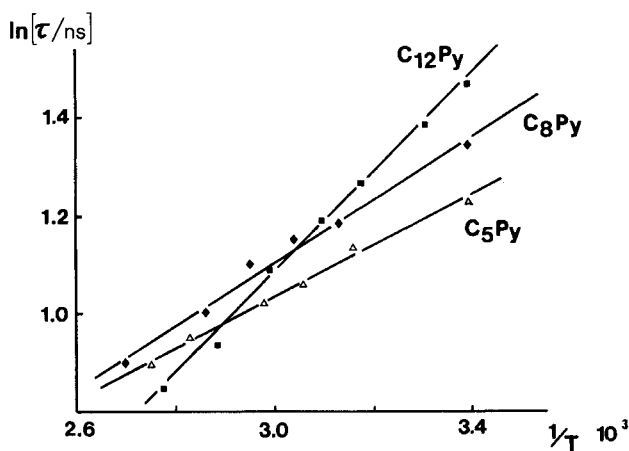


Figure 9. Temperature variations of the excimer lifetime obtained with the C_n Py liquid-crystalline phases; $\lambda_{\text{ex}} = 580$ nm, $\lambda_{\text{em}} = 700$ nm.

is given by

$$\tau = n\tau_h^0 \exp(E_M/RT).$$

We have found that only the excimer lifetimes determined in the liquid-crystalline phases of the C_n Py salts follow such a law, indicating that the excimers are mobile and that the monomer emission comes rather from the lattice defects. The activation energy for excimer migration for C_5 Py, C_8 Py and C_{12} Py is 0.046 eV, 0.061 eV and 0.087 eV respectively. These values are very close to those reported for molecular crystals [23].

Finally we can notice that the same photophysical properties (monomer and excimer fluorescence with the same spectra and similar lifetimes) characterize all of the C_n Py thin films examined. Four of them ($n = 4, 5, 8, 12$) are known to form columnar phases [6–8]. Since the photophysical properties are closely related to the geometrical parameters, our observations suggest that both C_2 Py and C_3 Py also have a columnar structure.

The elaboration of a theoretical model for one and multi dimensional energy migration is in progress in order to establish the experimental observation of high intracolumnar and low intercolumnar hopping rates in the liquid crystalline phases.

4. Conclusion

The study of the photophysical properties of the triaryl pyrylium salts substituted by six alkoxy chains has shown that:

- (i) in solution, when the chainlength increases both the fluorescence lifetimes and fluorescence yields increase;
- (ii) both monomer and excimer emission is observed with the pure compounds although excimer emission is predominant;
- (iii) both fluorescence spectra and fluorescence lifetimes of the pure compounds do not depend on the chain length suggesting that the columnar structure exists for all of the compounds examined;

- (iv) in the liquid-crystalline phases excimers are mobile and monomer emission comes rather from lattice defects;
- (v) the activation energy determined for excimer migration is very close to that given for molecular single crystals.

The authors are indebted to Dr. J. C. Mialocq for his permanent interest and to Dr. P. Davidson for helpful discussions.

References

- [1] MARKOVITSI, D., MOUALLEM, M., RIGAUT, F., and MALTHETE, J., 1987, *Chem. Phys. Lett.*, **135**, 236.
- [2] MARKOVITSI, D., TRAN-THI, T. H., BRIOIS, V., SIMON, J., and OHTA, K., 1988, *J. Am. chem. Soc.*, **110**, 2001.
- [3] MARKOVITSI, D., and LECUYER, I., 1988, *Chem. Phys. Lett.*, **149**, 330.
- [4] CHANDRASEKHAR, S., SHADASHIVA, B. K., and SURESH, K. A., 1977, *Pramana*, **9**, 471.
- [5] DESTRADE, C., GASPAROUX, H., FOUCHER, P., NGUYEN HUU TINH, MALTHETE, J., and JACQUES, J., 1983, *J. Chim. phys.*, **80**, 137.
- [6] STRZELECKA, H., JALLABERT, C., and VEBER, M., 1988, *Molec. Crystals liq. Crystals*, **156**, 355.
- [7] DAVIDSON, P., JALLABERT, C., LEVELUT, A. M., STRZELECKA, H., and VEBER, M., 1988, (a) *Liq. Crystals*, **3**, 133. (b) *Molec. Crystals liq. Crystals*, **161**, 395.
- [8] VEBER, M., Thèse d'Etat, Université de Paris Sud, France, 1987.
- [9] O'CONNOR, D. Y., and PHILLIPS, D., 1984, *Time-correlated Single Photon Counting* (Academic Press).
- [10] LAMPERT, R. A., CHEWTER, L. A., PHILLIPS, D., O'CONNOR, D. V., ROBERTS, A. J., and MEECH, S. R., 1983, *Analyt. Chem.*, **55**, 68.
- [11] MIALOCQ, J. C., 1982, *Chem. Phys.*, **73**, 107.
- [12] VAN DEN ZEGEL, M., BOENS, N., DAEMS, D., and DE SCHRYVER, F. C., 1986, *Chem. Phys.*, **101**, 311.
- [13] BALABAN, A. T., SAHINI, V. E., and KEPLINGER, E., 1960, *Tetrahedron*, **9**, 163.
- [14] WILT, J. R., REYNOLDS, G. A., and VAN ALLAN, J. A., 1973, *Tetrahedron*, **29**, 795.
- [15] WINTGENS, V., KOSSANYI, J., and SIMALTY, M., 1983, *Bull. Soc. Chim. Fr.*, II-115.
- [16] WINTGENS, V., POULIQUEN, J., KOSSANYI, J., WILLIAMS, J. L. R., and DOTY, J. C., 1985, *Polymer Photochem.*, **6**, 1.
- [17] TRIPATHI, S., SIMALTY, M., and KOSSANYI, J., 1985, *Tetrahedron Lett.*, **26**, 1995.
- [18] BERLMAN, I. B., 1965, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic Press).
- [19] BRUHAT, G., 1965, *Optique* (Masson & Cie), p. 309.
- [20] LECUYER, I., and MARKOVITSI, D. (unpublished results).
- [21] BAEYENS-VOLANT, D., and DAVID, C., 1985, *J. Phys., Paris*, **47**, 2141.
- [22] FORSTER, TH., 1969, *Angew. Chem. Int. Ed.*, **8**, 333.
- [23] YAKHOT, V., COHEN, M. D., and LUDMER, Z., 1979, *Adv. Photochem.*, **11**, 489.
- [24] WILLIAMS, L. R., and NELSON, K. A., 1987, *J. chem. Phys.*, **87**, 7346.
- [25] WEBER, M. J., 1971, *Phys. Rev. B*, **4**, 2932.
- [26] KLOPPFER, V., BAUSER, H., DOLEZALEK, F., and NAUNDORF, G., 1972, *Molec. Crystals liq. Crystals*, **16**, 229.
- [27] MIZUNO, K., and MATSUI, A., 1987, *J. Luminesc.*, **38**, 323.
- [28] LEVELUT, A. M., 1983, *J. Chim. phys.*, **80**, 149.