Recl. Trav. Chim. Pays-Bas 111, 507-510 (1992)

Intramolecular charge-transfer fluorescence of 1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine (fluoroprobe) as a sensor for phase transitions in the solid state

Leonardus W. Jenneskens^a *, Herman J. Verhey^b, Hendrik J. van Ramesdonk^b, Jan W. Verhoeven^b *, Kees F. van Malssen^c and Henk Schenk^c

^a Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

^b Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

^c Laboratory of Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WS Amsterdam, The Netherlands

(Received March 20th, 1992)

Abstract. As evidenced by temperature-dependent wide-angle X-ray diffraction (WAXD), the thermochromism of the continuous and time-resolved (nanosecond time scale) fluorescence behaviour of 1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine (fluoroprobe) dissolved in octadecyl octadecanoate is shown to be a highly sensitive probe for a phase transition in the solid state occurring in the latter.

Introduction

1, 1 - Phenyl - 4 - [(4 - cyano - 1 - naphthyl)methylene] piperidine (fluoroprobe**) displays a strong and highly solvatochromic charge-transfer (CT) fluorescence from a dipolar excited state $[D^{\ddagger}-A \cdot]^*$, which is populated by rapid photoinduced intramolecular charge separation after excitation^{1.2}. Recently, we have shown that the emissive behaviour of fluoroprobe, when dissolved in either amorphous³ or crystalline⁴ polymeric matrices, is markedly affected by the medium mobility of the matrix sites which accomodate the probe molecule. Temperature-dependent continuous and time-resolved fluorescence measurements showed that relaxation of the dipolar excited state $[D^{\ddagger}-A^{\ddagger}]^*$ becomes impaired on the photophysical time scale leading to fluorescence from non-relaxed excited states. In this paper we report some remarkable observations made during temperature-dependent continuous and time-resolved fluorescence measurements of solid solutions of fluoroprobe in crystalline octadecyl $[CH_3 - (CH_2)_{17} - O - (CO) - (C$ octadecanoate $-(CH_2)_{16}-CH_3$; m.p. 334K], which reveal that the emissive behaviour of fluoroprobe can be a sensitive probe or the occurrence of phase transitions in the solid state.



** Chemical Abstracts name: 4-[(1-phenyl-4-piperidinylidene)methyl]-1-naphthalenecarbonitrile.

Results and discussion

In Figure 1 the temperature dependence of the fluorescence maximum position of fluoroprobe in octadecyl octadecanoate is presented. In all cases, only one characteristic broad CT emission band was observed; the width and shape of the band remained nearly the same (FWHM 1875 cm⁻¹, red edge of the CT emission band). Upon heating, the fluorescence maximum initially undergoes a bathochromic



Figure 1. Temperature dependence of the CT fluorescence maximum of fluoroprobe dissolved in octadecyl octadecanoate as detected by continuous and time-resolved emission spectroscopy. From the latter measurements, maxima observed at a delay with respect to the excitation pulse of ≤ 5 ns ('initial') and ≥ 60 ns ('final') are indicated.

shift. This is in fact the normal behaviour, *i.e.* with increasing temperature relaxation pathways leading to a stabilization of the dipolar excited state $[D^{\perp}-A^{\perp}]^*$ will become available on the photophysical time scale. It should be noted, however, that in previous experiments with amorphous polymeric matrices, *i.e.* poly-(methyl methacrylate)³, a much less steep rise of the fluorescence maximum with temperature below the glass transition temperature was found. Even more unexpectedly, a pronounced hypsochromic shift of the fluorescence maximum with increasing temperature is observed in the temperature regime 20-30K below the melting point of the crystalline matrix resulting in a situation where the fluorescence in the mobile molten matrix occurs at a considerably shorter wavelength than in the solid matrix, around 300K! This implies that over a limited temperature range, i.e. 280-300K, the solid matrix exerts a stronger stabilizing effect on the dipolar excited state $[D^{\dagger}-A^{+}]^{*}$ of fluoroprobe than can be achieved by the same matrix in a mobile molten condition where the molecules are free to respond to the orienting effect of the dipolar field exerted by that excited state⁵. To gain insight in the dynamics of the relaxation of the dipolar excited state $[D^{2}-A^{-}]^{*}$ of fluoroprobe, temperature-dependent time-resolved fluorescence spectra were measured. In Figure 1 also the initial fluorescence maximum (λ_{init}), determined within 5 ns of laser excitation, and the final wavelength (λ_{fin}) reached after ca. 60 ns as a function of temperature are shown. While qualitatively both the $\lambda_{init.}$ and $\lambda_{fin.}$ show a behaviour analogous to that found in the continuous measurements, the temperature dependence of $\lambda_{\rm fin.}$ is much more pronounced. Thus, $\Delta \lambda = (\lambda_{\rm fin.} - \lambda_{\rm init.})$ changes considerably as the temperature changes, indicating that the dynamical reorganization of the dipolar excited state $[D^{\ddagger}-A^{\ddagger}]^*$ of fluoroprobe is markedly influenced by changes in temperature. This is further substantiated by a three-dimensional graphical representation of the temperature-dependent, time-resolved emissive behaviour of fluoroprobe dissolved in the octadecyl octadecanoate matrix (Figure 2). The results illustrate the complex temperature dependence of the dynamics⁶ underlying relaxation of the dipolar excited state $[D^{:}-A^{\cdot}]^{*}$ of fluoroprobe in the present matrix in the premelting temperature region. It should be stipulated that the observed changes in emissive behaviour of fluoroprobe con-

comitant with temperature are reversible for both the continuous and time-resolved fluorescence measurements! Although at first sight the results might be attributed to partial melting processes of the crystalline matrix, differential scanning calorimetry (DSC) clearly showed that there is only a homogeneous melting transition, which sets in at most 10K below the peak temperature (334K). No distinctive solid-solid transitions or gradual disorder, as would have been evidenced by a deviation of the DSC trace from the base-line below the melting point, could be observed. In addition, with polarization microscopy also a sharp melting trajectory of ca. 2K was found. Temperature-dependent IR spectroscopy revealed that, in the temperature region where the hypsochromic shift of the CT fluorescence of fluoroprobe occurs, octadecyl oactadecanoate is a crystalline compound (Figure 3; splitting of the CH₂-bending and in-plane-rocking vibration, *i.e.* 1472 cm⁻¹ and 1464 cm⁻¹ and 729 cm⁻¹ and 720 cm⁻¹, respectively, due to intermolecular interactions in the solid state, and a series of progression bands of the out-of-plane twisting and wagging vibrations of the CH₂ groups in the 1200-1350 cm region, which indicate an all-trans configuration of the aliphatic chains)⁷. Broadening of the sharp bands and complete loss of the splittings occurs only within 5K of the melting point. In passing, we wish to remark that the observed changes in the IR spectrum of octadecyl octadecanoate are reversible. These results show that in the temperature region in which the hypsochromic shift of the fluorescence maximum of fluoroprobe takes place, octadecyl octadecanoate is still a crystalline compound. Consequently, the hypsochromic shift cannot be attributed to the occurrence of partial melting of the solid matrix. Therefore, we anticipate that the hypsochromic shift of the fluorescence maximum of fluoroprobe is due to a phase transition of the matrix, which may escape detection by DSC⁸ and IR⁹ spectroscopy. To corroborate this interpretation temperature-dependent wideangle X-ray diffraction powder patterns (WAXD) of octadecyl octadecanoate were determined¹⁰. In agreement with available data for related, long-chain aliphatic esters, such as viny $|^{8a}$, ethy $|^{8b}$ and propy $|^{8c}$ octadecanoate, the straight alkyl chains of octadecyl octadecanoate crystallize in an orthorhombic subcell (WAXD short spacings at ca. 4.1 Å and 3.7 Å, Table I). The WAXD results indicate that, in the



Figure 2. Three-dimensional plot of the temperature-dependent, time-resolved fluorescence of fluoroprobe in octadecyl octadecanoate.



Figure 3. IR spectrum (range 1600–600 cm⁻¹) of octadecyl octadecanoate measures at T < 334K and T > 334K.

temperature range in which the hypsochromic shift of the CT fluorescence maximum of fluoroprobe occurs, octadecyl octadecanoate indeed undergoes a phase transition. At 318K, a moderate shift of the 3.7 Å short spacing to 3.8 Å sets in combination with a decrease in intensity. At 330K, this short spacing is absent. Furthermore concomitant with the changes of the 3.7 Å short spacing, a shift of the 4.14 Å short spacing to 4.2 Å takes place. This spacing, which is indicative for the formation of a hexagonal subcell, is still discernible in the WAXD powder pattern above 330K! It finally disappears upon complete melting of the matrix at 334K. It should be noted that the phase transition found for octadecyl octadecanoate upon heating, is common to many long-chain aliphatic compounds, which show a similar behaviour close to their melting points^{8,11}.

Conclusion

The thermochromism of the intramolecular CT fluorescence of fluoroprobe dissolved in octadecyl octadecanoate can be

Table I Relevant short spacings observed with temperature-dependent wide-angle X-ray powder diffraction for octadecyl octadecanoate in the temperature range 298–334K.

Temperature (K)	Short spacings	Short spacings [intensity ^a] (Å)	
298	3.73 [200]	4.14 (1450]	
308	3.73 [200]	4.14 [1450]	
318	3.75 [175]	4.14 [1400]	
328	3.78 [175]	4.14 [1350]	
329	3.80 75	4.17 [850]	
330		4.18 750	
331		4.18 [600]	
332	-	4.20 [450]	
333	-	4.20 [150]	
334 ^b			

^a Arbitrary units. ^b Melting point of octadecyl octadecanoate (cf. text).

attributed to a phase transition of the matrix sites, which takes place 20-30K below its melting point. Preliminary results indicate that the observed hypsochromic shift of the fluorescence maximum of fluoroprobe is also found in other matrices consisting of aliphatic esters, such as ethyl octadecanoate and octadecyl acetate. The sensitivity of the emissive behaviour of fluoroprobe in response to a phase transition of the solid matrix holds a promise for its application in the characterization of solid-state micro-environments. Further experiments directed to gain insight in the practical application of fluoroprobe are in progress.

Experimental

Preparation and characterization of octadecyl octadecanoate

Octadecyl octadecanoate was prepared by reaction of equimolar amounts of octadecanol and octadecanoyl chloride in dichloromethane. The aliphatic ester was purified by recrystallization; satisfactory NMR, MS and IR data were obtained. Differential scanning calorimetry (DSC) was done using a Mettler DSC 30, with a heating/cooling rate of 5K/min. Temperature-dependent IR spectra were measured on a dispersive Perkin–Elmer 983 spectrometer (resolution 4 cm⁻¹) using a home-built oven with temperature controller (accuracy 1K). For the temperature-dependent IR experiments a sample of octadecyl octadecanoate was applied between potassium bromide windows and molten *casu quo* recrystallized in the oven twice using a similar heating/cooling rate as in the DSC experiments before the measurement of the temperature-dependent dispersive IR spectra.

Continuous-fluorescence measurements

Continuous fluorescence spectra were measured on a Spex Fluorolog 2 spectrophotometer in front-face geometry, using dilute solid solutions of fluoroprobe (conc. < 1 mMol; λ_{exc} 310 nm). The spectra were corrected for the detector response. A broad CT fluorescence band was obtained whose maximum shifted as a function of temperature; the width and shape of the band remained nearly the same (FWHM 1875 cm⁻¹; red edge of the CT emission band).

Time-resolved fluorescence measurements

Temperature-dependent time-resolved fluorescence spectra were obtained using an excimer laser (XeCl, $\lambda_{exc.}$ 308 nm, FWHM *ca.* 10 ns) or excitation and observing the emission via a spectrograph with an electronically gated (gate width 5 ns) intensified diode-array

detector using dilute solid solutions of fluoroprobe (conc. < 1 mMol). The system (EG & G OMA-III) allows the observation time window to be delayed incrementally with respect to the excitation pulse. The time-resolved spectra were not corrected for the detector response.

Wide-angle X-ray powder diffraction

Wide-angle X-ray diffraction powder patterns were measured on a special diffractometer, dedicated to real-time diffraction and equipped with an RG & G diode-array position-sensitive detector and a PAAR sample holder.

Acknowledgements

We would like to thank Ir. A. J. Witteveen for experimental contributions and EG & G for providing part of the equipment.

References and Notes

- ¹ G. F. Mes, B. De Jong, H. J. van Ramesdonk, J. W. Verhoeven, J. M. Warman, M. P. de Haas and L. E. W. Horsman-van den Dool, J. Am. Chem. Soc. 106, 6524 (1984).
- ² R. M. Hermant, N. A. C. Bakker, T. Scherer, B. Krijnen and J. W. Verhoeven, J. Am. Chem. Soc. 112, 1214 (1990).
- ³ H. J. van Ramesdonk, M. Vos, J. W. Verhoeven, G. R. Mohlmann, N. A. Tissink and A. W. Meesen, Polymer 28, 951 (1987).
- ^{4a} L. W. Jenneskens, H. J. Verhey, H. J. van Ramesdonk, A. J. Witteveen and J. W. Verhoeven, Macromolecules **24**, 4038 (1991);

- ^bL. W. Jenneskens, J. P. B. van Deursen, H. J. Verhey, H. J. van Ramesdonk and J. W. Verhoeven, Appl. Fluor. Technol. 3, 11 (1991).
- ⁵ Although at first sight the similarity of the fluorescence maximum of fluoroprobe at low temperature and in the melt appears to be remarkable, it should be noted that solvation of its dipolar excited state $[D^{\pm}-A^{\pm}]^*$ may also become impaired due to thermal motion of the molten, mobile matrix molecules^{4a}; *cf.* also *P. Suppan* and *C. J. Tsaimis*, J. Chem. Soc., Faraday Trans. 2, 77, 1553 (1981).
- ⁶ Cf. K. Sienicki, S. Blonski and G. J. Durocher, J. Phys. Chem. 95, 1576 (1991).
- ^{7a} J. F. Rabolt, F. C. Burns, N. E. Schlotter and J. D. Swalen, J. Chem. Phys. **78**, 946 (1983);
- ^bM. Avram and G. H. Mateescu, Infrared Spectroscopy, Wiley-Interscience, New York and London, 1966, Chapter 2.
- ^{8a} Cf. N. Morosoff, H. Morawetz and B. Post, J. Am. Chem. Soc. 87, 3035 (1965);
- ^bS. Aleby, Acta Chem. Scand. 22, 811 (1968);
- ^cS. Aleby, Acta Chem. Scand. 22, 3146 (1968).
- ⁹ Although it may be argued that changes in the IR splittings are anticipated upon modification of the intermolecular interactions due to a phase transition, we would like to remark that the resolution (4 cm^{-1}) of the IR spectra is only modest. Consequently, subtle changes in the value of the IR splittings in the temperature regime 298-330K in which the hypsochromic shift of the CT emission of fluoroprobe occurs, may thus escape detection.
- ¹⁰ The WAXD powder pattern was obtained for pure octadecyl octadecanoate. We feel that the very low concentration of fluoroprobe (conc. < 1 mMol) used in the solid solutions will hardly affect the results. This is supported by the reversible nature of the observed temperature dependence of the emissive behaviour of fluoroprobe (cf. text).
- ¹¹ A. A. Scheurs, G. G. Bayle and W. M. Mazee, Recl. Trav. Chim. Pays-Bas 75, 513 (1956).