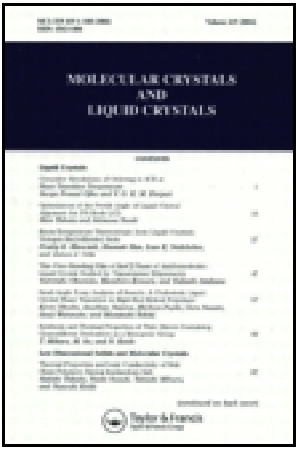

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photophysical Properties of a Lyotropic Discotic Liquid Crystal in the Isotropic Phase

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Version of record first published: 24 Sep 2006

To cite this article: Rhian Hughes, Alastair Smith, Richard Bushby, Bijan Movaghar & Neville Boden (1999): Photophysical Properties of a Lyotropic Discotic Liquid Crystal in the Isotropic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 547-557

To link to this article: http://dx.doi.org/10.1080/10587259908023801

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 547-557
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Printed in Malaysia

Photophysical Properties of a Lyotropic Discotic Liquid Crystal in the Isotropic Phase

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UV/VIS absorption, Raman, steady state and time resolved fluorescence spectroscopy have been used to characterise the photophysical properties of a triphenylene based lyotropic liquid crystal as a function of aggregate size in isotropic solution. The monomeric species, obtained in an organic solvent, has similar spectral properties to the isolated chromophore of triphenylene based thermotropic discotics. The process of self-assembly affects the photophysical properties of this system and we observe an increasing radiative lifetime with increasing aggregate size. These preliminary measurements can be interpreted in terms of a localised exciton that can move along the aggregates by hopping and that the ends of the aggregates may play an important role in promoting radiative relaxation.

Keywords: Lyotropic; discotic; triphenylene; self-assembly; fluorescence

INTRODUCTION

Systems that promote one-dimensional migration of charge and energy have attracted a great deal of attention due to their possible uses in molecular electronics and photonics. Particular interest has been shown in columnar liquid crystal phases as they posses highly anisotropic structures.

A comprehensive study into the photophysical properties of the thermotropic columnar liquid crystals, 2,3,6,7,10,11-hexa(n-alkoxy)-triphenylene, has been made by Markovitsi et al.[1-4] Experimental and theoretical investigation has presented an insight into the photophysical properties of the triphenylene based discotic mesogen as both an isolated chromophore and as part of a self-organised thermotropic structure. Singlet exciton migration in the organised thermotropic phases was investigated using Monte Carlo simulations assuming random walk hopping of a localised exciton. One dimensional transport was maintained for times of the order of a nanosecond.[4,5]

Energy transfer properties of lyotropic liquid crystals hold significant interest as they are analogous in some ways with biological systems,(for example the light harvesting complexes of cyanobacteria) and may present useful model systems. The triphenylene based lyotropic mesogen 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl) triphenylene (TP6EO2M) has been designed so that it has the ability to self-assemble into columnar aggregates and self-organise into columnar mesophases in aqueous solution.[6] One-dimensional linear self-assembly is a thermodynamically driven process, the extent of which is dependant upon concentration and temperature. A polydisperse distribution of aggregate sizes can be described for any given concentration. The relationship between concentration and average aggregate length has been investigated for dilute solutions using proton NMR.[7]

This unique system allows the investigation into how environmental conditions perturb the photophysical properties of a triphenylene based mesogen. We present preliminary photophysical characterisation of TP6EO2M in a monomeric form and for differing degrees of aggregation.

EXPERIMENTAL

TP6EO2M was synthesised as described previously.[8] The solvents, deuterium oxide (D_2O) and HPLC dichloromethane (DCM), were purchased from Fluorochem Ltd. and BDH respectively. Samples of varying concentration were prepared by successive dilution of a concentrated stock solution. Nitrogen was bubbled through the solvent prior to solution preparation to minimise dynamic quenching of fluorescence by triplet oxygen. All measurements were made in quartz cuvettes and at room temperature. The concentrations and temperatures used ensured that all measurements were made in the isotropic phase (see figure 2).

UV/VIS absorption spectra were obtained using a Perkin Elmer Lambda 2 spectrophotometer. Raman scattering measurements were made using a Renishaw Raman imaging spectrometer with incident light of 632.8nm. A Perkin-Elmer LS50-B fluorimeter was used to obtain steady state luminescence spectra. Modification of the equipment was necessary in order that efficient fluorescence collection could be ensured for optically dense samples (figure 1).

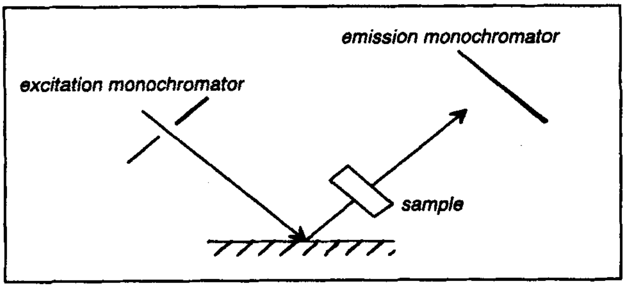

Figure 1. Fluorimeter setup in the modified arrangement.

The mirror and sample were placed in optimum positions to allow focusing of the exciting beam at the sample centre and efficient collection of fluorescence by the emission monochromator. A 290nm high pass filter was placed in front of the emission monochromator to eliminate scattered light. Sample thicknesses were varied in order that the optical densities of solutions of differing concentrations was kept constant and below a point of saturation (approx. 0.2 OD). This arrangement ensures excitation of a constant sample volume essential for quantum yield measurements which were made relative to 9,10 diphenyl anthracene in cyclohexane as a reference standard.

Fluorescence lifetime measurements were made using the time correlated single photon counting technique with a front face sample geometry. The second harmonic (532nm) of a mode locked NdYAG laser running at 76Mhz was used to pump a model 700 Coherent dye laser (Rhodamine 6G). The cavity dumped output of 4Mhz (564nm) was then frequency doubled using BBO to give the required excitation wavelength of 282nm. The fluorescence decays were obtained using an Edinburgh Instruments FL900-CDT with a micro channel plate photomultiplier tube (Hamamtsu R3809) providing an instrument function (FWHM) of approximately 70 ps. An ideal scatterer made of ground glass was used to obtain this function for fitting of the decays which was achieved by iterative reconvolution of the instrument function with an assumed decay law. A least squares fitting procedure determined the decay parameters, the quality of which were evaluated by the reduced χ^2 values, residuals and the autocorrelation function.

RESULTS

UV/VIS absorption, steady state fluorescence and time resolved fluorescence data are presented for isotropic solutions of TP6EO2M in deuterium oxide, D_2O. The phase diagram of this system is shown in figure 2. Investigation has been limited to a region of the isotropic phase corresponding to a temperature of 297K and to concentrations below 0.1wt % (~ 10^{-1}M). Increasing molar concentration is accompanied by an increase in aggregate size. Data have also been obtained for dilute solutions of TP6EO2M in DCM in order to obtain the characteristic behaviour of the monomeric species.

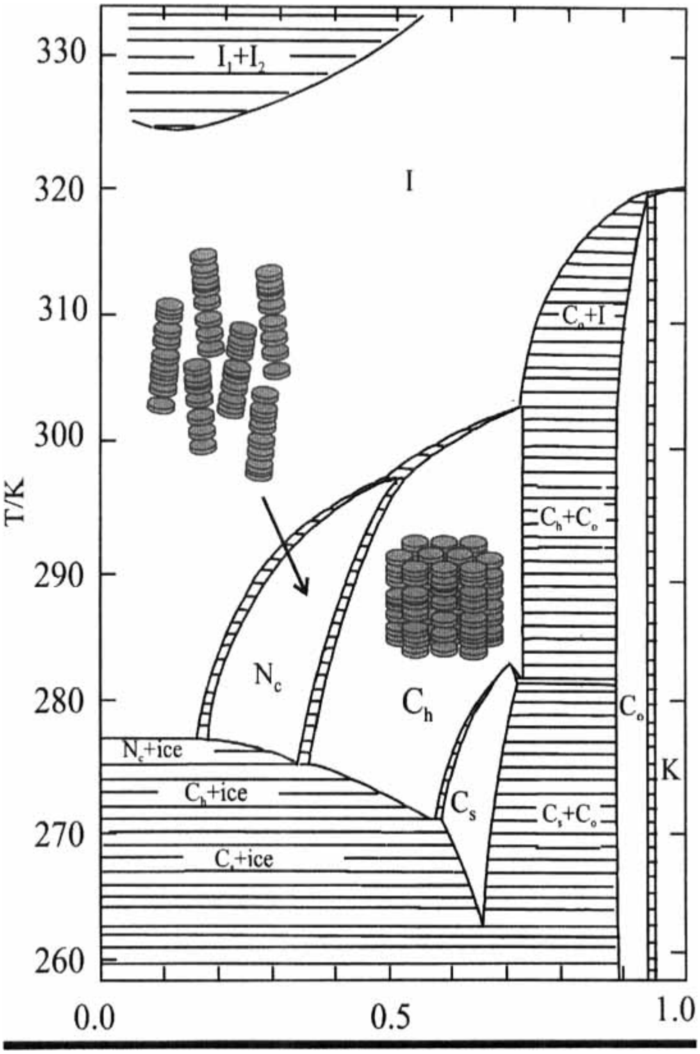

Figure 2. Phase diagram of TP6EO2M in D_2O

Figure 3 shows the absorption spectra of 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6}M solutions of TP6EO2M in D_2O and 10^{-4}, 10^{-5} and 10^{-6}M solutions of TP6EO2M in DCM. The same absorption peaks can be identified in each spectrum at approximate positions of 28986, 32573, 36101, 37313 and 38760 cm^{-1}.

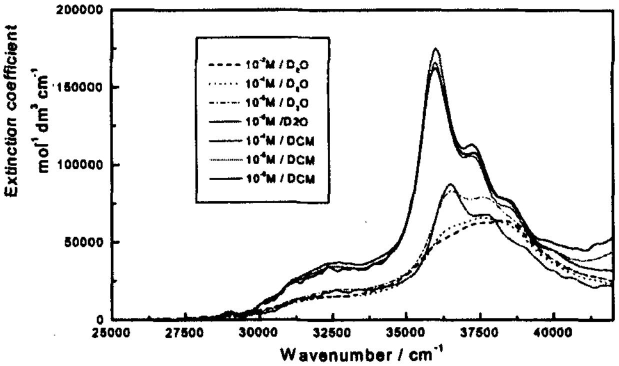

Figure 3. Absorption spectra of TP6EO2M in D_2O and DCM

Figure 4 shows the Raman spectra of the crystalline form of TP6EO2M. Two strong peaks are seen at 1397 cm^{-1} and 1640 cm^{-1} with a weaker peak at about 2900 cm^{-1} on a broad luminescence background.

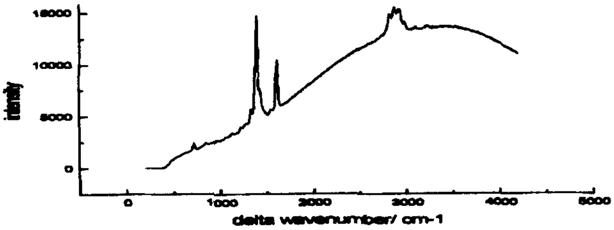

Figure 4. Raman spectra of TP6EO2M crystals

Figure 5 shows the fluorescence emission spectra of 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6}M solutions of TP6EO2M in D_2O and a 10^{-6}M solution of TP6EO2M in DCM for comparison. The main emission peak red shifts with increasing concentration by 474cm^{-1} over 3 the decades. No phosphorescence is observed for any sample in the isotropic phase, however, delayed fluorescence is seen in a degassed sample up to 50μs after excitation.

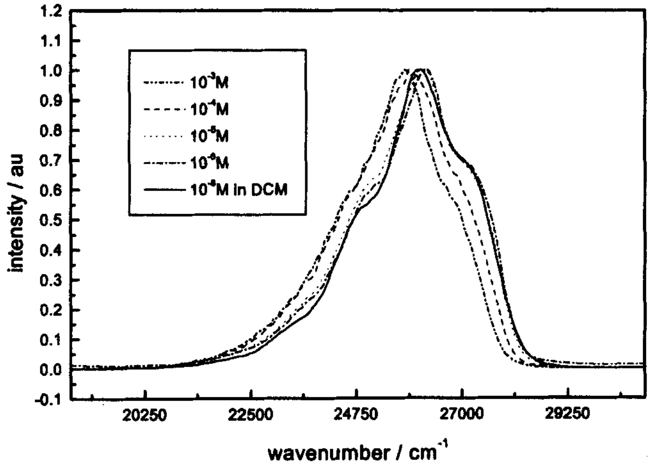

FIGURE 5. Steady state fluorescence spectra of TP6EO2M in D_2O and DCM

The solvent, excitation wavelength and concentration dependence of the fluorescence lifetimes of TP6EO2M are shown in table 1. All the fluorescence decays fitted well to a single exponential. The quantum efficiency has been measured for 4 concentrations and is largely unaffected by the aggregation process having a value of about 15% in each case.

Table 1. Quantum efficiency (QE), fluorescence and radiative lifetimes of solutions of TP6EO2M in D_2O and DCM at different excitation wavelengths (281nm and 315nm). Radiative lifetimes were calculated from the measured values of quantum efficiency and fluorescence lifetime.

Conc.	Fluor. Lifetime (ns) ex. λ 281nm	χ^2	Q.E.	Radiative lifetime (ns)	Fluor. lifetime (ns) ex. λ 315nm	χ^2	Radiative lifetime (ns)
D2O							-
10^{-1}M	18.50	0.92	-	-	18.50	1.13	
$5*10^{-2}$M	18.65	1.10	-	-	18.42	1.09	-
10^{-2}M	18.20	1.07	-	-	18.42	1.16	-
$5*10^{-3}$M	18.23	1.16	-	-	18.30	1.11	-
10^{-3}M	16.90	1.08	0.156	115	18.37	1.15	114
10^{-4}M	15.95	1.01	0.158	99.7	16.23	1.04	101
10^{-5}M	14.32	1.06	0.129	89.5	14.32	0.99	89.5
10^{-6}M	12.81	1.06	0.170	80.1	12.93	1.04	80.8
DCM							
10^{-4}M	8.90	0.96	-	-	-	-	-
10^{-5}M	8.30	1.07	-	-	-	-	-
10^{-6}M	8.30	1.19	-	-	-	-	-

DISCUSSION

To explain the results for the monomeric and aggregating TP6EO2M, it is useful to make a comparison with the spectra and theoretical (CSINDO) calculations on hexa(alkoxy)-triphenylene.[4]

The UV/VIS spectra of the TP6EO2M in DCM obeys the Beer - Lambert law at all wavelengths indicating that only monomeric species are present.

Aggregation effects are seen with increasing concentrations of TP6EO2M in D_2O and the Beer - Lambert law is not obeyed for the main absorption peaks. The slight redshift and higher relative extinction coefficient of the molecule in the organic solvent is attributed to a solvent effect.[9] The lowest energy absorption peaks at 28986 and 32573 cm^{-1} are attributed to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions which are symmetry forbidden but vibronically allowed. The main absorption peaks at 36101cm^{-1} correspond to the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions which are allowed and degenerate.

It can be seen that the spacing of the peaks in the $S_0 \rightarrow S_3/S_4$ transition is fairly even, suggesting that they arise from a vibronic series. Spacing of these peaks is around 1300 cm^{-1}which probably corresponds to the strong peak in the Raman spectrum at 1397cm^{-1} produced by C-C stretching.[10] We believe that the concentration dependence of the extinction coefficients of this vibronic series in the aqueous solvent should be attributed to an effect of aggregation on vibrational modes of the system resulting in a modification of the Franck - Condon factor for each vibronic peak.

Steady state fluorescence spectra exhibit the same spectral profile for all concentrations, solvents and excitation wavelengths. A small redshift of 0.058eV is seen with increasing aggregation, which is approximately 2kT, too small to suggest excited state delocalisation. One would not expect to see delocalised states in these systems as one does in conjugated polymers because the disc-disc separation is quite large (3.4 A). This does not exclude the possibility of energy migration due to the hopping of a localised exciton.

Time resolved emission spectra all fit well to a single exponential, indicating that one emission process is occurring. Fluorescence lifetimes are not dependent on excitation wavelengths indicating that fluorescence originates from the lowest energy $S_0 \rightarrow S_1$ transition.

The quantum efficiency has been shown to be independent of aggregation. However, since the fluorescence lifetime is increasing with increasing aggregation this implies that the radiative lifetime of the emitting species in the aggregate must also be increasing. This may be due to longer survival times of the mobile exciton in larger aggregates implying that there is a low defect concentration or that the ends of the aggregates act as defects causing relaxation and emission. The saturation of the increase in radiative lifetime at 10^{-3} M may be indicative of increased flexibility of longer aggregates introducing more defects into the middle of the columns. It is also possible that reduced vibronic coupling in larger aggregates could reduce the allowedness of the $S_0 \rightarrow S_1$ transition thus reducing the radiative rate.

CONCLUSION

The absorption and fluorescence spectra of the isolated chromophore of the triphenylene based lyotropic discotic liquid crystal TP6EO2M has the same spectral profiles as the isolated chromophore of equivalent thermotropic derivatives. The process of self-assembly modifies the photophysical properties but there is no evidence of a delocalised excited state. Aggregation appears to perturb the vibronic structure of the excited state of the molecule which may be an explanation for the decrease in the radiative rate with increasing aggregate size. However, in the picture of a mobile exciton, able to move up and down the aggregate, an increase in the radiative lifetime with increasing aggregate size could suggest that the ends of the aggregates are the only defect sites that promote radiative relaxation. The radiative lifetime appears to reach a maximum value at high concentrations when aggregate flexibility may be introducing more intra-columnar defects. These phenomena are the subject of further fluorescence quenching experiments currently underway.

References

[1] D. Markovitsi, F. Rigaut, M. Mouallem and J Malthete, Chem Phys. Letts, **135,** 236 (1987)

[2] D. Markovitsi, I. Lecuyer, and J Simon. Phys. Lett, **167** 467 (1990)

[3] D. Markovitsi, I. Lecuyer, P. Lianos and J. Malthete. Chem .Soc. Faraday Trans., **87** (11), 1785 -1790 (1991)

[4] D. Markovitsi, A. Germain, P. Mille, P Lecuyer, L. K. Gallos, P. Argyrakis, H. Bengs and H. Ringsdorf. J. Phys. Chem., **99,** 1005–1017 (1995)

[5] D. Markovitsi, H. Sigal, K. Lazaros, G. Argyrakis, P. Argyrakis, J. Phys. Chem., **100,** 10999–11004 (1996)

[6] N. Boden, R. J. Bushby, L. Ferris, C. Hardy and F. Sixl, Liquid Crystals, **1**(2), 109–111. (1986)

[7] J. Hubbard, Thesis, University of Leeds, U.K. (1997)

[8] N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge, M. V. Jeusudason, Liquid crystals, **15**(6), 851 – 858 (1993)
[9] N. Boden, R. J. Bushby, J. Clements, R. Luo, J. Mater. Chem., **5**(10), 1741–1748 (1995)
[10] L. Colangeli, V. Mennella, G.A. Baratta, E. Bussoletti and G. Strazzulla, Astrophysical Journal, **396,** 369–377 (1992)