



Technical Report
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Photophysics of Cyanine Dyes Adsorbed onto Surfaces

TMR Large-Scale Facilities Access Programme

LF Vieira Ferreira et al

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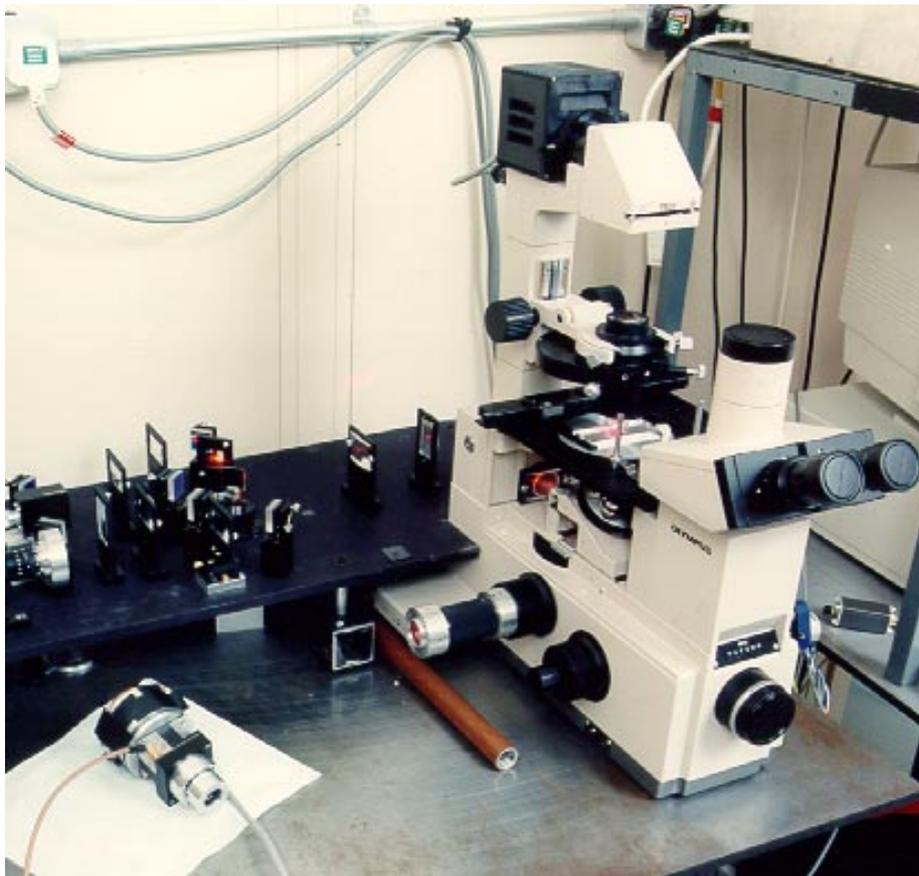
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**Photophysics of Cyanine Dyes
Adsorbed onto Surfaces:
Sub-Nanosecond Fluorescence Lifetime
Measurements of 3,3'-Diethyloxadicyanine
Iodide and Photoisomer**

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Instituto Superior Tecnico, Lisbon, Portugal

**An experiment performed with funding from the
TMR Large-Scale Facilities Access Programme
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**Access to Lasers at the Central Laser Facility
Rutherford Appleton Laboratory
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LF Vieira Ferreira and AS Oliveira,
Centro de Química-Física Molecular, Complexo I, IST, 1096 Lisboa Codex, Portugal

K Henbest
Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

DR Worrall and F Wilkinson
Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

Report prepared by CN Danson and G Booth
CLF, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

SUMMARY

This report describes the experiment entitled 'Photophysics of Cyanine dyes on Surfaces'; carried out at the Central Laser Facility (CLF) from the 6th to the 20th January 1997. The experiment, funded by the Framework IV Large-Scale Facilities Access Scheme, was proposed by Prof. LF Vieira Ferreira, Centro de Química-Física Molecular, Complexo I, IST, 1096 Lisboa Codex, Portugal, and carried out by visiting researchers from the Institute. They were supported by researchers from the Central Laser Facility, Rutherford Appleton Laboratory.

Experimental Results

- The photo physics of 3,3'-Diethyloxadicarbocyanine iodide (DODCI) adsorbed onto swollen microcrystalline cellulose was investigated.
- Two fluorescence emissions band have been observed and assigned. One was due to singlet excited momers and a second new emission, seen at high laser fluences, was due to the formation of a photoisomer.
- The DODCI stays entrapped between the polymer chains and nonradiative pathways for deactivation are reduced, the lifetimes of the excited states were measured using time resolved fluorescence lifetimes techniques.
- The fluorescence lifetimes of the excited states are longer lived in a swollen cellulose matrix. The photoisomer emission especially lives an order of magnitude longer than in homogeneous media.

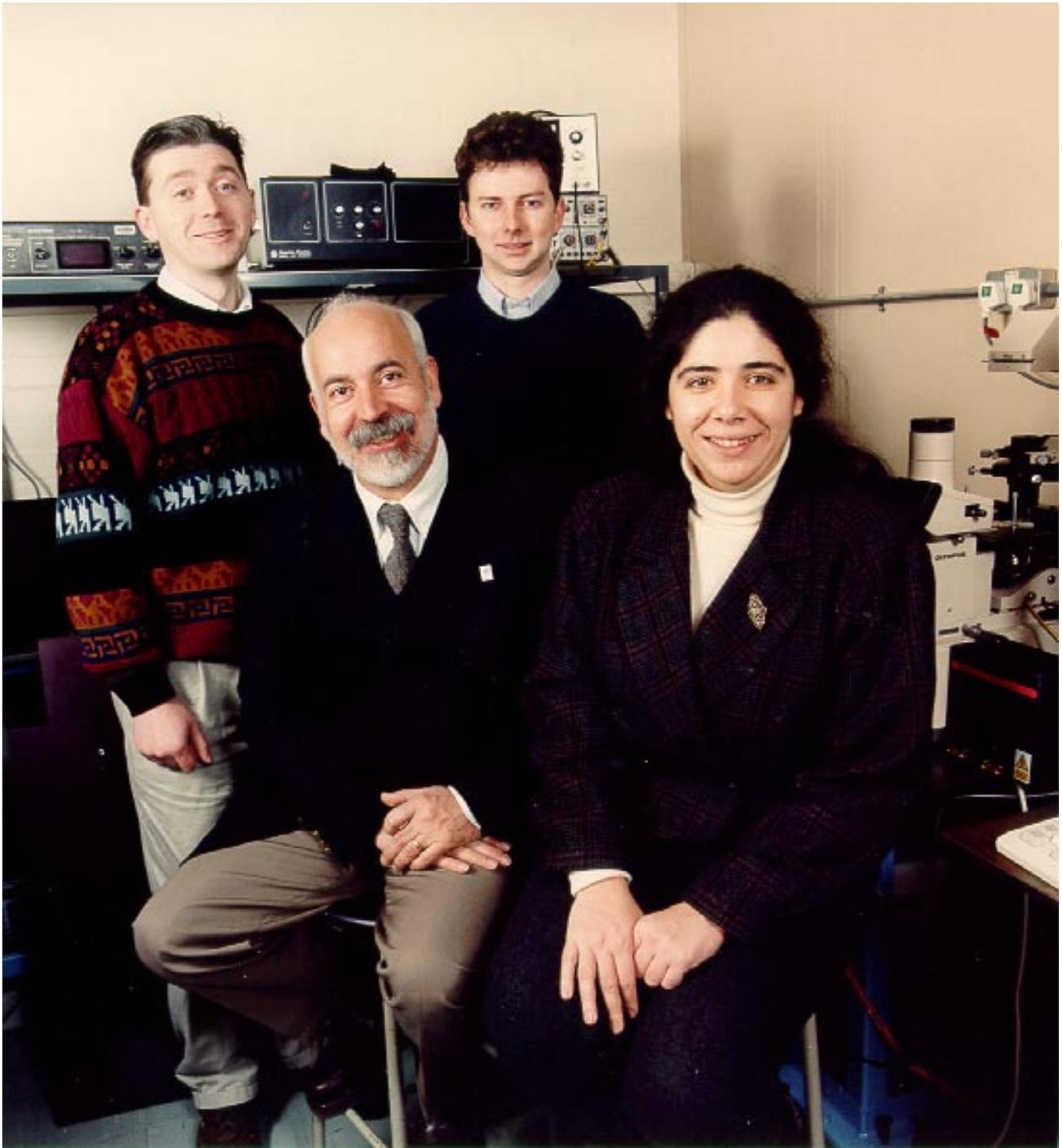
Arising Publications

'Photophysics Of Cyanine Dyes Adsorbed Onto Surfaces: Sub-Nanosecond Fluorescence Lifetime Measurements Of 3,3'-Diethyloxadicarbocyanine Iodide And Photoisomer.'

L.F. Vieira Ferreira, A.S. Oliveira, K. Henbest, D.R. Worrall, F. Wilkinson

Central Laser Facility Annual Report, RAL-TR-97-045

The CLF makes beam time at its facilities available to European Researchers with funding from DG-XII, CEC under the Large-Scale Facilities Access Scheme. For further information contact Dr. Chris Edwards at the CLF. Tel: (0)1235 445582, e-mail: c.b.edwards@rl.ac.uk



Clockwise from top left:

F. Worrall, K. Henbest, A.S. Oliveira, L.F. Vieira Ferreira

Photophysics Of Cyanine Dyes Adsorbed Onto Surfaces: Sub-nanosecond Fluorescence Lifetime Measurements of 3,3'-Diethyloxadicyanin Iodide and Photoisomer

INTRODUCTION

3,3'-Diethyloxadicyanin iodide (DODCI) is commonly used as saturable absorber for mode-locking dye lasers and as a laser dye for pulsed operation, tuneable around 660 nm. In recently published work [1] we described the behaviour of this dye when adsorbed onto a natural polymer, microcrystalline cellulose. In the range of concentration under study (from 0.005 to 25 μmol of dye per gram of cellulose) this dye exhibits sandwich type ground state dimers (H aggregates) and the degree of aggregation is dependent on the degree of hydration of the sample.

Both steady state and laser-excited fluorescence emission are dependent on the concentration of the dye on the surface of cellulose. For very low loadings of the dye only singlet excited monomers (M^*) emit while for higher loadings a second emission band was observed superimposed on the normal monomer emission and peaking at about 655 nm. This emission was seen when high laser fluences were used (~ 40 mJ per pulse and per square centimetre) [1]. Similar effects were reported for 2,2'-carbocyanin iodide adsorbed onto the same substrate [2].

Previously reported solution studies [3] have shown that DODCI monomer M^* and photoisomer N^* fluorescence emissions were detected simultaneously from concentrated solutions of the dye in ethanol both with picosecond and microsecond laser pulses. When the energy content of the excitation pulse was reduced by calibrated neutral density filters, the N^* fluorescence became weaker and the fluorescence spectra became more like M^* . Our recent report [1] shows this sharp new emission of the dye adsorbed onto microcrystalline cellulose for laser excitation and also a similar emission band (broader in this case) for the same samples obtained with a spectrophotometer.

The present study is a continuation of this work. Sub nanosecond lifetime measurements were performed for dry samples of DODCI adsorbed onto microcrystalline cellulose ranging

from 0.02 to 10.0 micromoles of dye per gram of the substrate, to evaluate both M* and N* lifetimes.

EXPERIMENTAL

Ground-state absorption spectra and steady-state or laser induced fluorescence emission spectra of powdered samples were obtained using the methods and apparatus described in references [1,2] and references therein.

Sub-nanosecond lifetime measurements of DODCI adsorbed onto microcrystalline cellulose was made by the use of a fluorescence microscope described in detail in reference [4]. Dye laser excitation pulses were approximately 10 ps halfwidth. The excitation wavelength used in this work was 580 nm and the dye laser pulse repetition rate was 0.8 kHz. In some cases band pass filters were used to separate M* emission from the excited photoisomer and neutral density filters to reduce laser energy. Data was recorded every 250 ps after excitation using a 500 ps time gate.

RESULTS AND DISCUSSION

Steady-state fluorescence spectra of three dry samples exciting with a 450W Xenon lamp at 530 nm are presented in figure 1. Spectra were obtained with full lamp intensity and also with a reduction of the exciting light to 20% by the use of a neutral density filter.

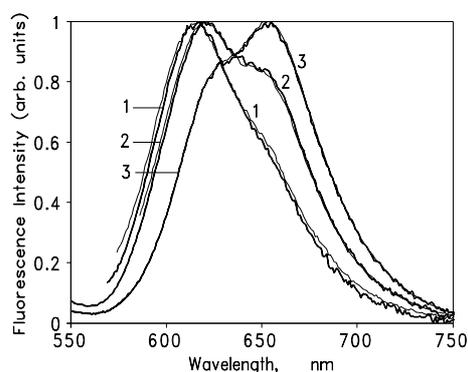


Figure 1 Steady-state emission spectra from dried samples of DODCI on microcrystalline cellulose, excited at 530 nm ----- full lamp 20%. Sample concentration: (1) 0.05, (2) 0.30 and (3) 4.2 $\mu\text{mol g}^{-1}$.

The perfect superposition of the two spectra for each sample suggest that M and N are already formed in the ground state and that emission spectra reflect the relative ground-state population independently of the number of photons used to excite the sample.

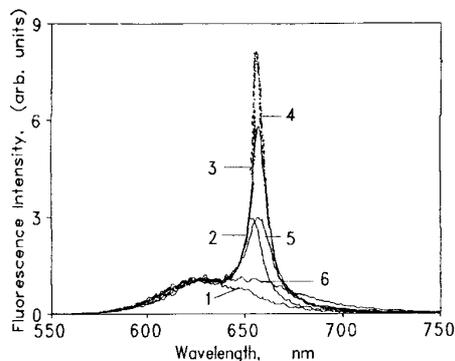


Fig.2 Laser induced fluorescence spectra for DODCI adsorbed onto microcrystalline cellulose, exciting at 532 nm and as a function of the dye concentration. Sample concentration is: (1) 0.02, (2) 0.05, (3) 0.10, (4) 0.30, (5) 1.0, (6) 4.2 $\mu\text{mol g}^{-1}$.

A powerful Nd:YAG pulsed laser was used (8ns excitation pulse width at 532 nm, ~ 40 mJ per pulse) and the obtained emission spectra are shown in figure 2. The photoisomer emission maximum peaks at ~ 655 nm (the same maximum as in figure 1, curve 3), but an intense peak instead of a broad band exists now. This was interpreted as amplified spontaneous emission (ASE) acting to narrow the metastable photoisomer emission on cellulose [1]. Figure 3 shows some of the fluorescence decay curves obtained with a 10 ps laser excitation as a function of the sample concentration.

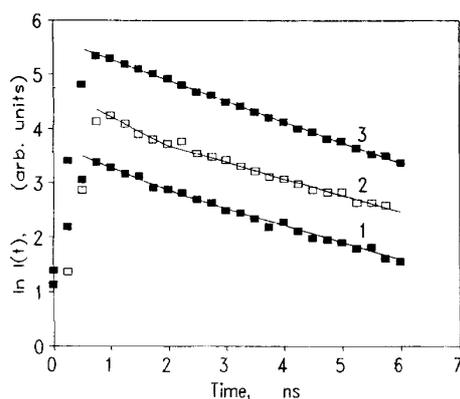


Figure 3 Fluorescence decay curves for DODCI adsorbed onto microcrystalline cellulose, exciting at 580nm and as a function of the dye concentration. Sample concentration is: (1) 0.02, (2) 0.30 and (3) 4.20 $\mu\text{mol g}^{-1}$.

In this system, a dichroic filter was used to separate laser excitation from fluorescence and the intensified CCD only detects $\lambda \geq 625$ nm. This obviously means that N* emission decay is amplified when compared with M* emission decay. At low loadings, two emissions were detected and as the concentration of DODCI increases, N* becomes predominant.

The decay curves presented in figure 3, together with data from Table 1, clearly show that the excited monomer lifetime is 1.6 ± 0.1 ns and that of the excited photoisomer is 2.7 ± 0.1 ns.

Table 1 Lifetimes of singlet monomer and photoisomer of DODCI adsorbed onto microcrystalline cellulose.

<i>Conc./ mmolg⁻¹</i>	0.02	0.05	0.10	0.30	0.50	1.0	4.2	10
<i>t_{N*}/ns</i>	2.70	2.78	2.73	2.77	2.75	2.65	2.63	2.67
<i>t_{M*}/ns</i>	1.68	1.59	1.64	1.56	-	-	-	-

These values can be compared with $\tau_{N^*}(\text{ethanol}) = 330$ ps [3] and $\tau_{M^*}(\text{ethanol}) = 1.25$ ns [5] at room temperature.

In conclusion, when cellulose matrix is swollen by the use of ethanol as solvent for sample preparation (see references [1,2] and references therein), DODCI stays entrapped between the polymer chains and nonradiative pathways for deactivation (internal conversion and trans-cis isomerization) are reduced, not only for M* but especially for N* which lives about one order of magnitude longer than in homogeneous media.

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