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Photophysics of Cyanine Dyes on Surfaces: Time Resolved Transient Absorption Spectra and Lifetime Measurements

TMR Large-Scale Facilities Access Programme

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TMR Large-Scale Facilities Access Programme**

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SUMMARY

This report describes the experiment entitled 'Photophysics of cyanine dyes on surfaces: Time resolved transient absorption spectra and lifetime measurements'; carried out at the Central Laser Facility (CLF) from the 26th Jan to the 14th Feb 1998. The experiment, funded by the Framework IV Large-Scale Facilities Access Scheme, was proposed by Dr L Ferreira, Centro de Química-Física Molecular, Portugal and carried out by visiting researchers from the Centre. They were supported by researchers from the UK from Loughborough University, Leicestershire and the Central Laser Facility, Rutherford Appleton Laboratory.

Experimental Results

- The photophysics of cyanine dyes adsorbed on microcrystalline cellulose was studied under different excitation energies.
- The experiments revealed that vastly different fluence and intensity thresholds exist for spectral narrowing of fluorescence for fs and ns excitations and luminescence properties strongly depend on dye aggregation.
- This provides insight into the narrowing mechanism which is ascribed to the onset of superfluorescence originating from photoproducts.

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

Arising Publications

Journal Publications and Reports:

L.F. Vieira Ferreira, P. V. Cabral, P. Almeida, A.S. Oliveira, M.J. Reis, A.M. Botelho Do Rego - "UV/VIS Absorption and Luminescence and X-Ray Photoelectron Spectroscopic Studies of Rhodamine B Covalently Bound to Microcrystalline Cellulose" *Macromolecules*, 31 (1998) 3936.

LF Vieira Ferreira, AS Oliveira, K Henbest, R Worrall, F Wilkinson 'Photophysics of Cyanine Dyes Adsorbed onto Surfaces: Sub-Nanosecond Fluorescence Lifetime Measurements of 3,3'-Diethyloxadicarbocyanine Iodide and Photoisomer', RAL-TR-98-012

L.F. Vieira Ferreira, A.S. Oliveira, P. Matousek, M. Towrie, A.W. Parker, D.R. Worrall, F. Wilkinson "Photochemistry on Surfaces: Transient Absorption Measurements Thiocarbocyanine Monomers and Photoisomers Adsorbed onto Microcrystalline Cellulose" - manuscript in preparation, (1998).

Seminars and Posters:

A.S. Oliveira, L.F. Vieira Ferreira, F. Wilkinson, D.R. Worrall, "Photophysics of Cyanine Dyes on Surfaces: A New Emission Observed with Laser Excitation", "Jornadas de Fotoquímica do ITQB", Oeiras (Abril 1997).

L.F. Vieira Ferreira, P. V. Cabral, P. Almeida, A.S. Oliveira, A.M. Botelho Do Rego - "Estudos Espectroscópicos de Absorção e Luminescência no UV/Vis. e de Fotelectrão de Raios X de Rodamina B Ligada Covalentemente a Celulose Microcristalina" ,"5º Encontro Nacional de Fotoquímica". Universidade do Minho, Braga (Outubro 1997).

L.F. Vieira Ferreira, P. V. Cabral, P. Almeida, A.S. Oliveira, M.J. Reis, A.M. Botelho Do Rego - "UV/VIS Absorption and Luminescence and X-Ray Photoelectron Spectroscopic Studies of Rhodamine B Covalently Bound to Microcrystalline Cellulose", Summer Meeting at the CLF, June (1998).

LF Vieira Ferreira, AS Oliveira, KH Henbest, DR Worrall, F Wilkinson - "Photophysics of Cyanine Dyes Adsorbed onto Surfaces: Sub-Nanosecond Lifetime Measurements of 3,3'-Diethyloxacarbo-cyanine Iodide and Photoisomer" - RAL CLF Annual Report, (1997) 143.

Photophysics of Cyanine Dyes on Surfaces: Time Resolved Transient Absorption Spectra and Lifetime Measurements

INTRODUCTION

In recently published work ¹⁻⁵ we describe the behaviour of several cyanine dyes adsorbed onto a natural polymer, microcrystalline cellulose. In the range of concentrations under study (from 0.005 to 25.0 μmol of dye per gram of cellulose) several cyanines exhibit sandwich type and/or head to tail ground state aggregates. The aggregation is dependent on dye structure and on the degree of hydration of the sample.

Steady-state and laser induced fluorescence emission may provide different emission spectra. For several cyanines under study and for low loadings, only monomers (M^*) emit and the two emission spectra are equal within experimental error, while for higher loadings a new emission (N^*) was observed arising from a photoisomer generated by the absorption of a initial photon, and excited by the absorption of a second photon. Supralinear dependencies on laser fluence were detected in several cases ¹⁻⁵.

Apart from this new photoisomer emission, an amplified spontaneous emission process (ASE) was claimed to exist explaining the narrow emission peaks of 3,3'-diethyloxadicyanine iodide both in acetonitrile solution and adsorbed onto microcrystalline cellulose ².

The present study is a continuation of this work. Transient absorption measurements with picosecond resolution were performed for dry and wet samples of 3,3'-diethylthiacarbocyanine iodide (TCC) and 3,3'-diethyl-9-methylthiacarbocyanine iodide (9-Me-TCC) adsorbed onto microcrystalline cellulose ranging from 0.02 to 15.0 μmol of dye per gram of the substrate, to evaluate both M^* and N^* lifetimes under the excitation of a powerful picosecond laser system.

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 refs. 1,2 and references therein. Fluorescence quantum yields for TCC and 9-Me-TCC were determined at room temperature using the method described in ref. 7, with rhodamine 101 adsorbed onto microcrystalline cellulose as reference ($\phi_F=1.0$).

Transient absorption measurements of 9-Me-TCC and TCC adsorbed onto microcrystalline cellulose were made by the use of a pump and probe time resolved system, operating with two independent tuneable optical parameter amplifiers described in detail in ref. 6. Excitation pulses were approximately 1 ps halfwidth. The pump wavelength was 534 nm and the probe was 800 nm. The repetition rate was 1.0 kHz and the energy was about 3 μ J per pulse.

Fluorescence emission spectra were also obtained under the same pumping conditions, using as detector a CCD camera coupled to a double grating monochromator ⁶. The luminescence produced by the excitation of the picosecond laser was collected with a microscope objective and guided to the entrance of the monochromator by an optical fiber.

RESULTS AND DISCUSSION

Ground state absorption spectra of several samples of TCC and 9-Me-TCC adsorbed onto microcrystalline cellulose are presented in Figure 1, where we plot reflectance as a function of wavelength. For both dyes, low loadings simply show monomer absorption and for high loadings (curve 5) 9-Me-TCC exhibits a new absorption band peaking at about 610 nm, which corresponds to J aggregate formation.

Steady-state fluorescence spectra of TCC samples, excited with a 450W Xenon lamp at 530 nm simply show monomer emission, in contrast with a pulsed excitation (nitrogen laser or YAG laser) which produces both photoisomer emission and ASE. These results are similar to those obtained for 3,3'-dimethylthiacarbocyanine iodide as recently reported ⁴.

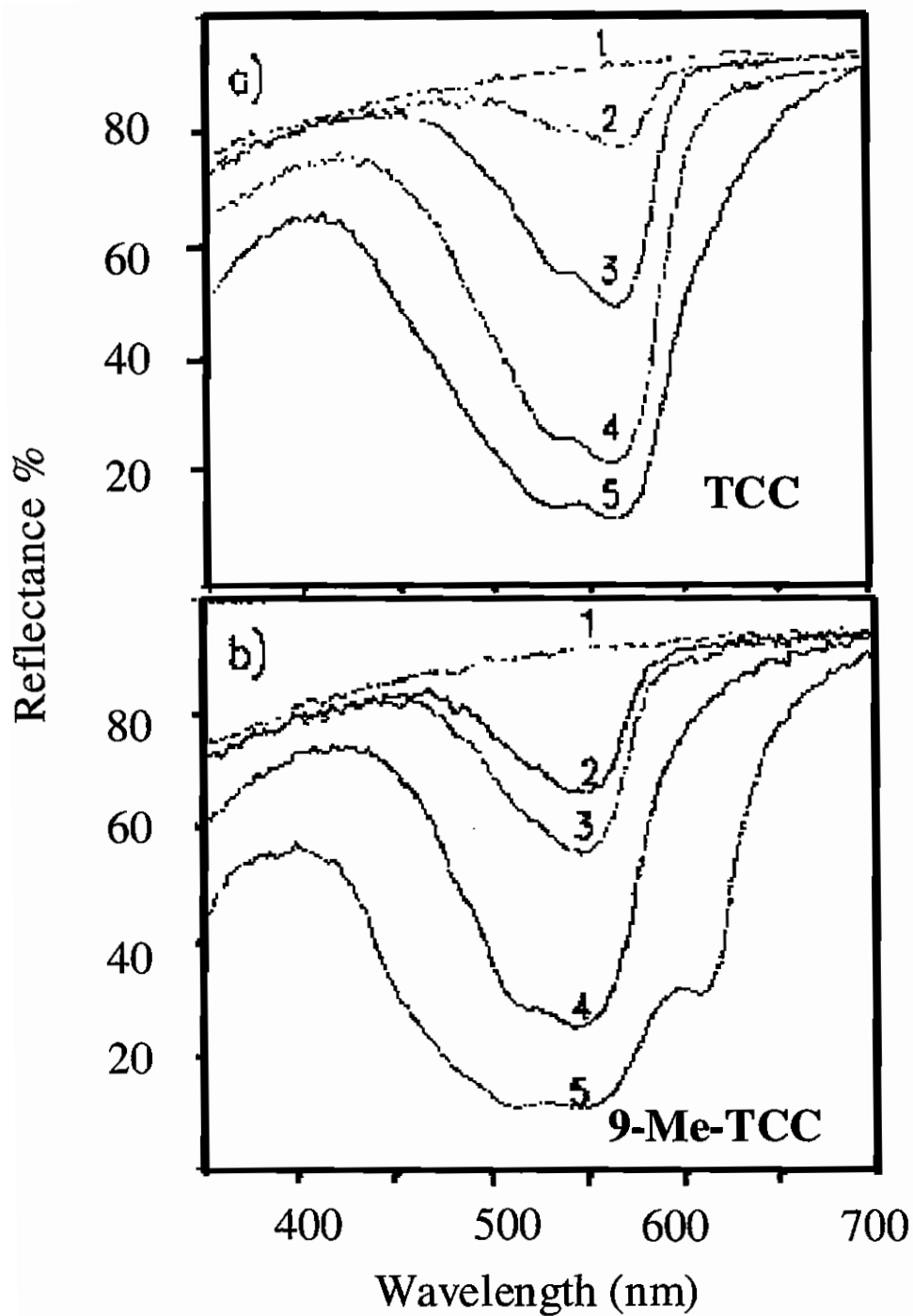


Figure 1 - Reflectance spectra for samples of a) TCC and b) 9-Me-TCC adsorbed onto microcrystalline cellulose. Sample concentrations: (1) 0, (2) 0.05, (3) 0.10, (4) 1.0 and (5) $5.2 \mu\text{molg}^{-1}$.

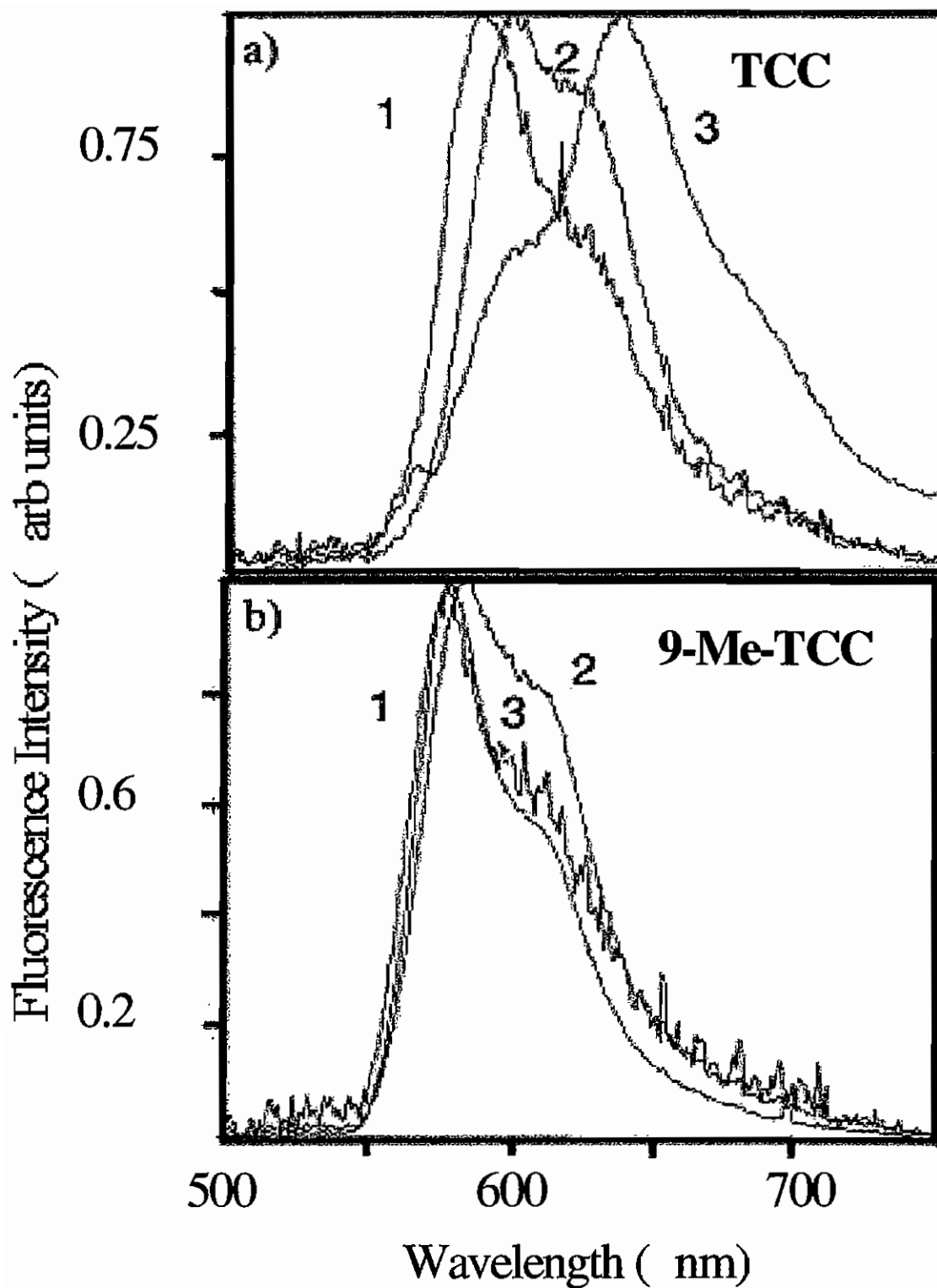


Figure 2. Laser induced fluorescence spectra for samples of a) TCC and b) 9-Me-TCC adsorbed onto microcrystalline cellulose, exciting at 532 nm and as a function of the dye concentration.

Sample concentrations: (1) 0.08, (2) 0.5, (3) 10.0 $\mu\text{mol g}^{-1}$.

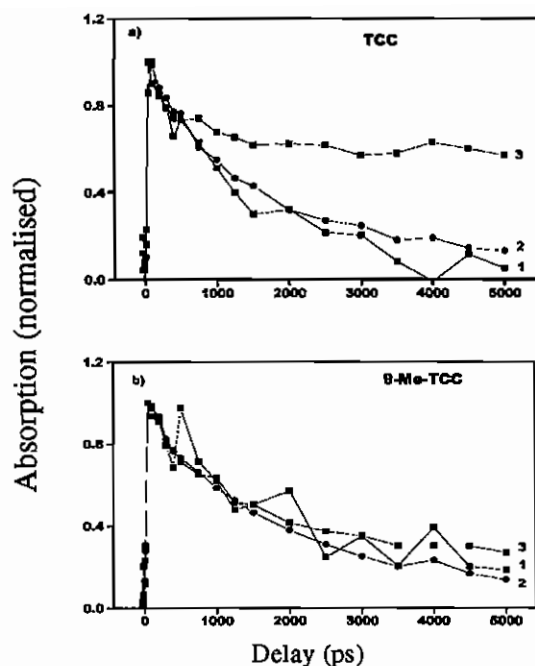


Figure 3 - Transient absorption decay curves for samples of a) TCC and b) 9-Me-TCC adsorbed onto microcrystalline cellulose, exciting at 532 nm and as a function of the dye concentration. Sample concentrations: (1) 0.08, (2) 0.5, (3) 10.0 $\mu\text{mol g}^{-1}$.

Picosecond laser excitation, with a repetition rate of 1 kHz clearly creates different populations of emissive species, as illustrated in Figure 2. Strong photoisomer emission is clearly seen for TCC, while for 9-Me-TCC, mainly monomers emit, without ASE in both cases. Transient absorption measurements exhibit quite different behaviour for the two dyes, as shown in Figure 3 where a long-lived transient absorption attributable to a photoisomer is only observed in the case of TCC.

In conclusion, we have shown that the luminescence properties for the two thiacyanine dyes under study are strongly dependent on dye aggregation (J aggregate formation reduces photoisomerization), and on the characteristics of the excitation source.

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