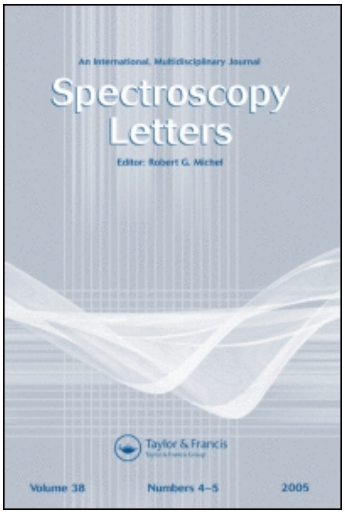

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A Thermal and Photostable Reference Probe for Q_f Measurements: Chloroform Soluble Perylene 3,4,9,10-Tetracarboxylic Acid-bis-N, N-Dodecyl Diimide

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A THERMAL AND PHOTOSTABLE REFERENCE PROBE FOR Q_f MEASUREMENTS: CHLOROFORM SOLUBLE PERYLENE 3,4,9,10-TETRACARBOXYLIC ACID-bis-N,N`-DODECYL DIIMIDE

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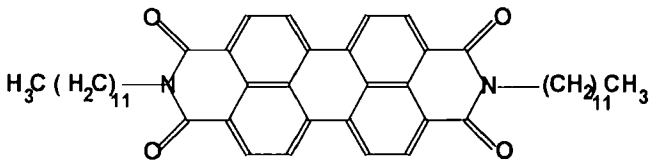
Abstract - The synthesis of a chloroform soluble perylene 3,4,9,10-tetracarboxylic acid-bis-N,N`-dodecyl diimide via condensation of perylene 3,4,9,10-tetracarboxylic dianhydride and 1,12-diamino dodecane is described. The thermal analysis is shown thermal stabilities above 400°C. Thermal and photostable dye is measured to have a fluorescence quantum yield of unity, $Q_f = 1.00$, in chloroform solutions. Perylene bis-dodecyl diimide is an ideal reference probe for fluorescence quantum yield measurements in 500-650 nm region and a reliable soluble photosensitizer for solar photochemical applications.

INTRODUCTION

We have shown recently that the fluorescence quantum yields of synthesized perylene diimides vary drastically (Q_f= 0.04-0.96) on N-aryl(alkyl) substitution[1]. The low solubilities of these compounds(~10-20 mg/lt, only in acetonitrile and dimethylformamide) may have been responsible of Q_f variations through aggregate formations. The insolubility of these highly thermal and photostable structures, limits the applications as photosensitizers in photochemical reactions. Literature in major gives results on solid state investigations. Graser and Hadicke[2] and later Duff et. al.[3] have determined the effect of the N-alkyl group on photoconductivity by solid state absorption of N,N`-dialkyl diimides.The photoconductivity of these dyes in the visible region and polymorphism has been demostrated in solid state films[4]. Electron acceptor capacity of perylene diimide photosensitizers were proven by Wasielewski[5].

We now report a novel synthesis and spectral characteristics of perylene 3,4,9,10-tetracarboxylic acid-bis-N,N`-dodecyl diimide for solution studies.



EXPERIMENTAL

A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (185.2 mg, 0.472 x 10^{-3} mol), dodecylamine (175 mg, 0.944 x 10^{-3} mol) , *m*-cresol (20 ml) and isoquinoline (2 ml) was stirred at 80 ^{0}C for 1 hour. Then the solution was heated at 120 ^{0}C for 1 hour, temperature was raised to 160 ^{0}C, heated for 2 hours and finally at 200 ^{0}C for 5 hour. The warm solution was poured into acetone (250 ml), the diimide which precipitated was recovered by filtration through a Buchner funnel and dried in vacum oven. In order to remove the traces of *m*-cresol and isoquinoline, the solid was extracted with acetone in a soxhlet apparatus for 24 hours.The residue was dissolved in chloroform and re-precipitated

in 250 ml acetone. The precipitate was sublimized at 350°C on salt-ice cooled glass surface. The yield was 307 mg, 95 %.

$C_{48}H_{58}N_2O_4$	Calc.	C 79.30	H 8.04	N 3.85
	Found	C 78.89	H 8.04	N 3.81

The mass spectra was taken with a Fision VG Zab MS instrument.The ir spectra were recorded with Kbr pellets using a Perkin Elmer 983 IR spectrophotometer.The UV absorption spectra were measured with a DMS 90 Varian UV spectrophotometer and the emission spectra with a spex fluorolog, in Merck grade chloroform. Rhodamine 101 was used as reference probe for fluorescence quantum yield measurements. Dupont 951 TGA, and Dupont 910 DSC instuments are used for thermal analysis studies. Proton nmr spectra were recorded with a Bruker AC 200 L 200 Mhz NMR spectrometer.

RESULTS AND DISCUSSIONS

The molecular structural analysis of perylene bi-dodecyl diimide was done by mass and ir spectral analysis. The molecular peak is being detected at 727 m/e as a base peak, the loss of a dodecyl group peak at 559 m/e and perylene dicarboxylium ion at 307 m/e.The ir spectrum of the diimide has shown carbonyl bands at 1697 cm^{-1} and 1650 cm^{-1} , CH_2 and CH_3 stretchings at 2853 cm^{-1}, 2920 cm^{-1} and 2960 cm^{-1}.

The perylene bis-dodecyl diimide is found to dissolve most in chloroform solutions, 180 mg/l. The perylene diimides, synthesized and studied earlier were practically insoluble in chloroform[1]. Solubility in chloroform capabled the nmr analysis. Proton nmr spectrum in $CDCl_3$ is , δ ppm: methyl, 0.87 (t, J=5.6 Hz), CH_2-N, 4.20 (t, J=6.5 Hz), Ar-H, 8.62-8.70 (AB-dd, J_{AB}=8.0 Hz), remaining methylene protons are observed as multiplets at 1.2-1.4 ppm. The UV spectrum of dodecyl diimide is shown higher molar absorbtivity constants in respect to perylene aryl diimides reported earlier[1] (table 1). Fluorescence quantum yield of the perylene bis-dodecyl diimide in chloroform, calculated with respect to reference probe rhodamine 101, is 1.00 at emission spectrum of 485 nm excitation wavelength (figure 1). Thermal analysis of dodecyl diimide shows a weight loss above

Table 1: The UV absorbtion data of perylene bis-N,N`-dodecyl-diimide in chloroform[a].

λ^{b}_{max}	$\varepsilon^{c}_{max}(x10^{4})$
460	1.74
490	4.74
526	7.62

[a] At concentration 0.246 x 10^{-4}m; [b] λ(nm); [c] ε (m^{-1} cm^{-1}).

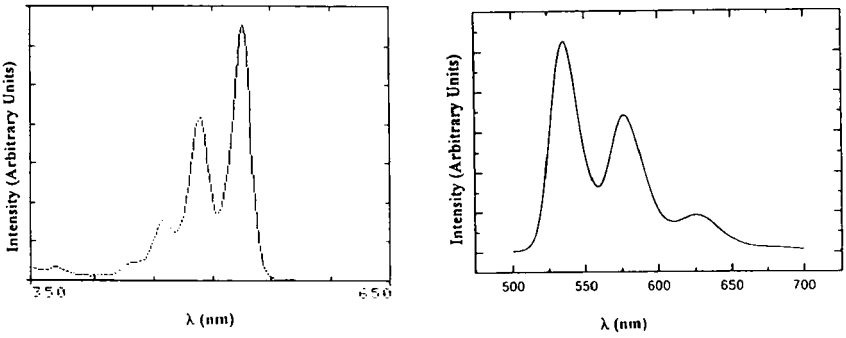


Figure1 : Absorbance and fluorescence (λ = 485 nm) spectra of perylene 3,4,9,10-tetracarboxylic acid-bis-N,N`-dodecyl diimide, in chloroform.

400°C. Thermal stability and known high photostabilities of perylene bis-alkyl diimides, proves that perylene bis-dodecyl diimide is superior in respect to rhodamine 101 and other reference probes of fluorescence quantum yield measurements, and a reliable soluble photosensitizer for solar photochemical applications

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