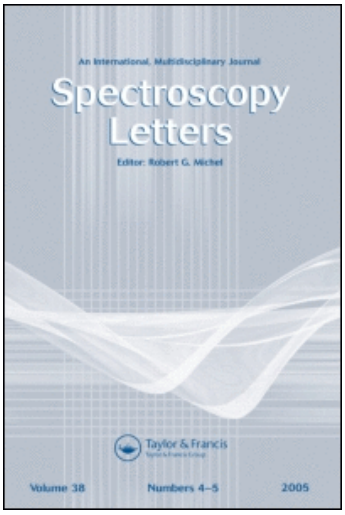

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Synthesis of a New Thermal and Photostable Reference Probe for Q_f Measurement in Aqua: Water Soluble N,N'-*bis*-(2-Hydroxy-4-benzoic Acid)-3,4,9,10-perylenebis(dicarboximide)

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SYNTHESIS OF A NEW THERMAL AND PHOTOSTABLE REFERENCE PROBE FOR Q_f MEASUREMENT IN AQUA: *WATER SOLUBLE* N,N`-BIS-(2-HYDROXY-4-BENZOIC ACID) -3,4,9,10-PERYLENEBIS(DICARBOXIMIDE)

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Abstract – N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) is synthesized from perylene 3,4,9,10-tetracarboxylic dianhydride and 4-amino-3-hydroxy benzoic acid in 90% yield. Together with the photostability the dye is also very stable thermally.The fluorescence quantum yield is measured as one, $Q_f = 1$.The diimide dissolves in water at PH = 8 completely.The diimide is an ideal reference probe for fluorescence quantum yield measurements in 500-650 nm region and an attractive photosensitizer for the photoreactions occur in water.

INTRODUCTION

Perylene 3,4,9,10-tetracarboxylic bisimides draw attention with their high thermal and photostability. The fluorescence quantum yield is about unity for the most derivatives[1].The high fluorescence potential of the dyes could not be realized due to their low solubility in most of the organic solvents. The solubility of the perylene dyes may increase with attached bulky aliphatic groups[2].Langhals et. al.[3] have determined the effect of N-alkyl substituents to solubility as a function of chain length.Yukinori Nagao and Takahisa Misono[4] proposed that the pressure of a higher chain in the N,N`-dialkyl perylenebis(dicarboximide) appeared to lower the decomposition temperature.However we have shown recently that perylen-3,4,9,10-tetracarboxylic acid-bis-N,N`-dodecyl

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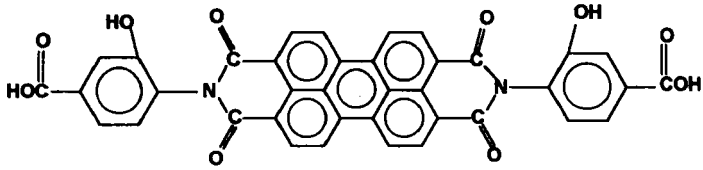
diimide degradation temperature as 400 °C[1].The perylene-3,4,9,10-tetracarboxylic acid-bis-(N,N'-dodecylpolyimide) has enough solubility in some of the common organic solvents to make spectroscopic and photochemical studies succesfully[1] .The polymer decomposes at 475 °C.

Brian A. Gregg et. al.[5] has proven perylene-SnO_2 system as a promising dye-semiconductor combination . New synthetic routes for the functionalized perylenes in high yields has been reported recently by Peter Schlichting, Ulrike Rohr and Klaus Müllen[6].

Reported herein is a water soluble perylene 3,4,9,10-tetracarboxylic bisimide which we offer it as a singlet state photosensitizer for photoreactions occur in aqua.



EXPERIMENTAL

A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1 g, 2.55 x 10^{-3} mol), 4-amino-3-hydroxy benzoic acid (0.781 g, 5.1 x 10^{-3} mol), m-cresol (40 ml) and isoquinoline (4 ml) was stirred at 80 °C for 1 hour. Then the solution was heated at 120 °C for 2 hours, the temperature was raised to 160 °C and kept for 2 hours. The reaction was then completed by stirring at 200 °C for another 10 hours. The warm solution was poured into 250 mL of acetone, and the precipitate was filtered out and dried at 100 °C under vacuum. The crude product was washed with N,N-dimethylformamide in order to get rid off the unreacted amine and then treated with acetone in a Soxhlet apparatus for 24 hours, in order to remove high boiling solvents, m-cresol and isoquinoline. The product is further purified by column separation (silica gel, chloroform/acetone/formic acid 10:0.5:1). Yield 90% bordeaux powder, m.p. greater than 400 °C. The product could not be sublimed up to 500 °C.–R_f (silica gel, chloroform/acetone/formic acid 10:0.5:1) = 0.4.

$C_{38}H_{18}N_{10}O_2$	Calc.	C 68.89	H 2.74	N 4.23
	Found	C 68.52	H 2.74	N 4.12

Perylene-3,4,9,10-tetracarboxylic dianhydride, pure grade, isoquinoline, 97% and 4-amino-3-hydroxy benzoic acid were obtained from Aldrich. M-cresol, 98%, was supplied by Fluka, and used without further purification. N,N-dimethylformamide, acetone, chloroform and formic acid were purchased from Aldrich.

The ir spectra were recorded with Kbr pellets using a Bruker IFS66 IR spectrometer. UV spectrophotometric measurements were carried out with an UV-2102 PC UV-VIS Scanning spectrophotometer and emission spectra with a Spex fluorolog, in Merck grade chloroform. Rhodamine 101 was used as reference probe for fluorescence quantum yield measurements. Elemental analyses were obtained from Carlo Erba-1106 C,H,N analyzer.

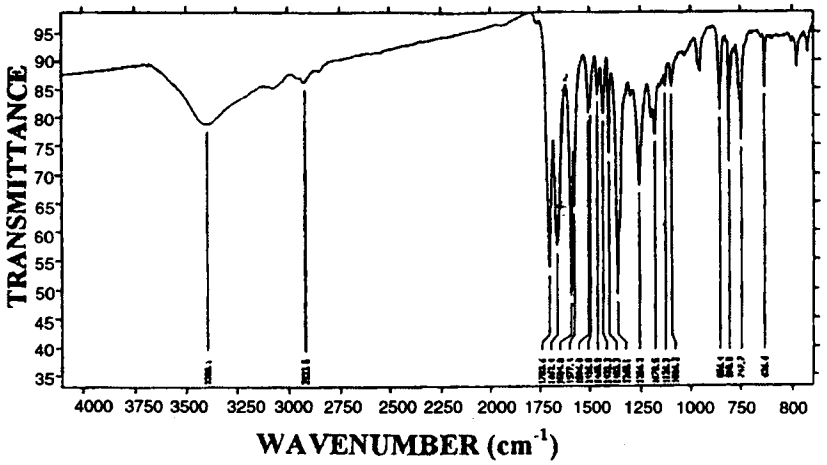


Figure 1 : IR spectrum of N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis (dicarboximide).

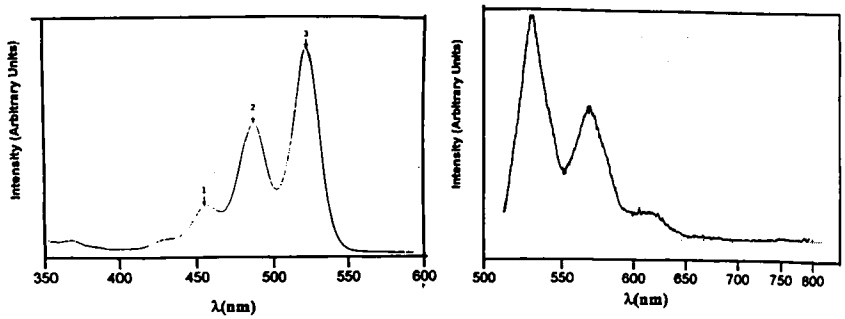


Figure 2 : Absorbance and fluorescence (λ_{exc} = 485 nm) spectra of N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) in chloroform.

Table 1: The UV absorption of N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) in chloroform[a].

λ^{b}_{max}	ε^{c}_{max}
455.5	17550
487.5	36630
524.0	54790

[a]At concentration 1 x 10^{-5} m; [b]λ(nm); [c]ε_{max}(m^{-1} cm^{-1}).

RESULTS AND DISCUSSION

The structure was confirmed by elemental analysis, absorption spectrum, emission spectrum and IR spectrum. Mass spectra of N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis (dicarboximide) was not obtained because of its low volativity. The diimide could not be sublimed even at the temperature up to 500 °C. The ir spectrum of the diimide has shown hydrogen bonded –O-H stretching at 3399.1 cm^{-1} as a weak and broad band, aromatic CH stretching at 2923 cm^{-1}, imide carbonyl stretching at 1703.6 and 1662 cm^{-1} (Fig.1).

The UV spectrum shows typically three absorption bands at 460-524 nm for the highest occupied bonding energy levels of perylenediimides[1-6](Fig.2). The UV spectrum of the diimide is shown lower molar absorptivity constants in respect to perylene alkyl diimides reported earlier[1] (Table 1). The fluorescence quantum yield measured in reference to the rhodamine 101, $\Phi_f = 1.0$ in chloroform (Fig.2).

The emission spectrum at an excitation wavelength of 485 nm is shown in Fig.2. The emission spectrum shows three bands at 527.7, 567, 615.9 nm. No excimer emission was observed.

N,N`-bis(2-hydroxy-4-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) dissolves in water at PH = 8. With its superior stability to heat and light and strong fluorescence it should be very attractive photosensitizer for photoenergy transfer and electron transfer reactions occurred in water. Also it is a perpect reference probe for fluorescence quantum yield measerements in water.

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