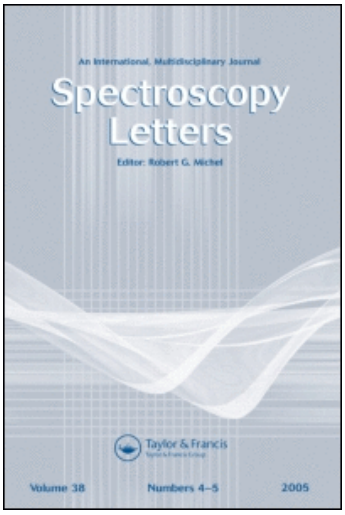

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF WATER SOLUBLE PERYLENE TETRACARBOXYLIC DIIMIDE DERIVATIVES

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF WATER SOLUBLE PERYLENE TETRACARBOXYLIC DIIMIDE DERIVATIVES

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ABSTRACT

Two new perylene dye, N,N′bis(4-hydroxyphenyl)-3,4,9,10 perylenebis (dicarboximide) **(1)** and N,N′-bis-(3,3,5,5-tetramethyl piperidine)-3,4,9,10-perylenebis (dicarboximide) **(2)** have been synthesized. They are both soluble in water. A limited number of water soluble perylene dyes published in literature have been obtained in pure grade only with column chromatography. For this reason they are not useful for certain applications. The N,N′-bis-(3,3,5,5-tetramethyl piperidine)-3,4,9,10-perylenebis (dicarboximide) derivative is obtained in high purity with high yield. Solubility of dyes, **(1)**

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and **(2)** were measured as 4.4×10^{-5} g/ml and 5.1×10^{-3} g/ml respectively in distilled water at pH: 7. The solubility of N · N′-bis-(3,3,5,5-tetramethyl piperidine)-3,4,9,10-perylene-bis (dicarboximide) was increased with decreasing pH. The chemical and photochemical stabilities of **1**, and **2** are very high. The fluorescence quantum yields of compounds are different (0.053 **(1)**, 0.110 **(2)**). The report includes the electronic absorption and emission spectra, extinction coefficients and fluorescence quantum yields.

Key Words: Perylene dye; Water solubility; Photosensitizer; Electron acceptor

INTRODUCTION

N,N′-Dialkyl-(diaryl) imides of perylenetetracarboxylic acids are important dyes or pigments of high lightfastness and thermal as well as photochemical stability. The high fluorescent quantum yield, up to 100% is a very important property of Perylenediimides. They are used in plastics and dye industry, in optical data storage, as laser dyes, in fluorescence solar collector[1,2]. Some Perylene derivatives show photoconductivity in the solid state[3,4]. They are ideal standards for measuring fluorescence quantum yields[5,6] in 500–650 nm region. They are applicable as fluorescent labelling[7], as bathochromically shifted fluorescence[8]. The nonsymmetrical perylene dyes generally show a tendency to aggregate[9,10]. A black polyimide, Perylene-3,4,9,10-tetracarboxylic acid-bis-(N,N′-dodecylpolyimide) may be an excellent camouflage paint due to its ir reflectivity and higher thermal stability comparing to perylene diimides[11]. Despite their great advantages, perylene diimides suffer from their limited processability due to poor solubility in organic solvents. Introducing long-chain secondary alkyl groups (swallow-tail substituents) into the dyes[12,13] enhances solubility. Heinz Langhals has synthesized firstly the water soluble perylene diimides[14]. Limited number of water-soluble perylene diimides reported, are obtained analytically pure grade with chromatographic methods[15]. It is therefore of prime interest to obtain an easily prepared water-soluble perylene dye. The perylene derivatives (see Fig. 1) N,N′bis(4-Hydroxyphenyl)-3,4,9,10-Perylenebis(dicarboximide) **(1)** and N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis(dicarboximide) **(2)** are all soluble in water.

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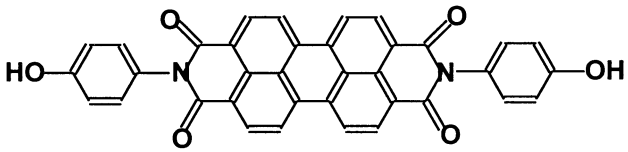

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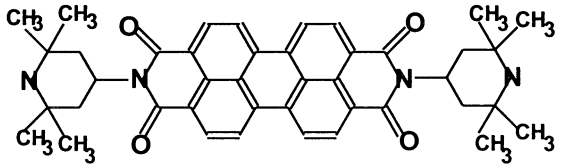

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Figure 1. Structural formulae of N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) **(1)** and N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) **(2)**.

EXPERIMENTAL

Measurements

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 270. UV-VIS absorption spectra were recorded on a Varian Cary 100 spectrophotometer. The ir spectra were recorded with KBr pellets using a Bruker IFS 66 (FT-IR) spectrophotometer. Mass spectra were recorded on a Finnigan MAT 311A instrument. Emission spectra were recorded on a Spex fluorolog. Elemental analyses were obtained from Carlo Erba-1106 C, H, N analyzer. Chromatographic separations were done with flash chromatography.

Solvents and Reagents

Perylene-3,4,9,10-tetracarboxylic dianhydride, pure grade, isoquinoline, 97%, m-Cresol, 98%, 4-aminophenol, 98%, and 4-amino-2,2,6,6-tetramethyl piperidine were obtained from Aldrich. All solvents used for column chromatography were distilled before use.

Synthesis

N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) (1): A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1 g,

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2.55×10^{-3} mol), 4-aminophenol (1.2 g, 11×10^{-3}), 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 150 °C and kept for 3 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 treated with acetone in a Soxhlet apparatus for 24 hours, in order to remove unreacted 4-aminophenol and high boiling solvents, m-cresol and isoquinoline. The crude product is further purified by column separation (silica gel, chloroform, methanol, acetic acid 15:5:4), $R_F = 0.56$. 0.8 g (54.8%) black powder, m.p.greater than 400 °C is obtained. The product could not be sublimed up to 400 °C under −3 mbar pressure. It was dissolved completely in concentrated sulfuric acid with a navy-blue color. The pigment was insoluble in common NMR solvents; the spectrum, which was taken in d-pyridine, was not excellent due to the poor solubility. However it was consistent with the proposed structure.

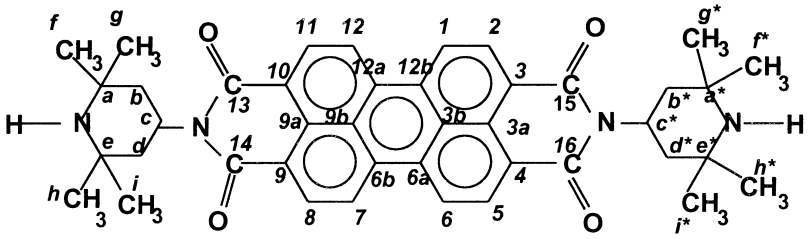
N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10 Perylenebis (dicarboximide) (2): A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1 g, 2.55×10^{-3} mol), 4-amino-2,2,6,6-tetramethyl piperidine (5 g, 3.1996×10^{-2} mol), m-cresol (40 ml) and isoquinoline (4 ml) was stirred at 80 °C for 1 hour. Then the solution was heated at 120 °C for 2 hour, the temperature was raised to 160 °C and kept for 2 hour. The reaction was then completed by stirring at 200 °C for another 10 hour. 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 ethanol in order to get rid of the unreacted amine and then treated for 1 hour with 10% NaOH in order to remove unreacted perylene dianhydride. In order to remove high boiling solvents, m-cresol and isoquinoline, the crude product was treated with ethanol in a Soxhlet apparatus for 24 hour. 1.5 g (90%) brown-red powder, m.p. greater than 400 °C was obtained. The perylene dye showed solubility, in water (PH: 7); 5.1×10^{-3} g/ml, in ethanol; 0.8×10^{-3} g/ml, in water (PH:8.2); 4.4×10^{-3} g/ml. The product was dissolved completely in concentrated sulfuric acid with a violet-pink color.

Characterization

N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) (1). Yield: 54.8%, color: black, m.p > 360 °C, Rf (silica, chloroform/methanol/acetic acid 15:5:4): 0.56, IR: ν (KBr pellets)/cm^{-1} 3432, 2931, 1707, 1639, 1559, 1415, 1339, 1270, 1124, 1021, 915, 809, 643 cm^{-1}. UV-VIS: λ_{max} (DMF)/nm (ε/mol^{-1} cm^{-1}) 454.00 (14430), 486.00 (28490), 522.20

(40240). Fluorescence: λ_{max} (DMF)/nm 533.91, 577.80, 620.82. $Q_f = 0.053$. MS: m/z: 574 (M^-), 503, 335, 153. ^{1}H NMR (250 MHz, pyridine-d_5): 8.7 (Ar-H). ^{13}C NMR (252 MHz, pyridine-d_5): δ: 150.4, 135.8, 123.9 (Ar-C). $C_{36}H_{18}N_2O_6$: Calcd. C 75.26, H 3.16, N 4.88; found C 75.37, H 3.12, N 4.76.

N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10 Perylenebis (dicarboximide) (2). Yield: 90%, color of the diimide: brown-red, m.p > 360 °C, R_f (silica, chloroform/acetone/formic acid 10:10:2): 0.58. IR: ν (KBr pellets)/cm^{-1} 3449, 2972, 1690, 1652, 1594.3, 1577.4, 1487.6, 1435.9, 1404.9, 1383.8, 1340.8, 1258, 1170.8, 1127, 810, 746, 674.5. UV-VIS: λ_{max} (DMF)/nm (ε/mol^{-1} cm^{-1}) 458.5 (28950), 488 (67150), 524 (89550). Fluorescence: λ_{max} (DMF)/nm 537.62, 577.97, 622.04. Q_f: 0.110 MS: m/z 669 (M+1), 652, 622, $C_{42}H_{42}N_4O_4$: Calcd C 75.65, H 6.35, N 8.40; found C 75.36, H 6.22, N 8.23.



^{1}H NMR: δ_H (250 MHz, $CCl_3D+C_2DF_3O_2$, 5:3) 8.8221 (H*11*, H*8*), 8.7894 (H*2*, H*5*), 8.7894 (H*12*, H*7*), 8.7701 (H*1*, H*6*), 5.8 (H*c*, H*c**), 2.3119 (1H*b*, 1H*d*), 2.2954 (1H*b**, 1H*d**), 2.2868(1H*b*, 1H*d*), 1.9835 (1H*b**, 1H*d**), 1.9304 (H-N), 1.7090 (H*f*, H*h*, H*f**, H*h**), 1.5330 (H*g*, H*i*, H*g**, H*i**). ^{13}C NMR: δ_C (252 MHz, $CCl_3D+C_2DF_3O_2$, 5:3) 163.018 (c*15*), 162.324 (c*16*), 161.631 (c*13*), 160.938 (c*14*), 135.969 (c*3*, c*4*, c*9*, c*10*), 133.209 (c*2*, c*5*, c*11*, c*8*), 129.588 (c*3a*),126.644 (c*9a*), 124.567 (c*1*, c*6*, c*12*, c*7*), 122.563 (c*9b*), 116.642 (c*3b*), 112.125 (c*6a*, c*6b*), 107.607 (c*12a*, c*12b*), 60.430 (c*a**, c*e**), 60.336 (c*a*, c*e*), 44.782 (c*c*, c*c**), 37.141 (c*b*, c*d*, c*b** , c*d**), 30.595 (c*f*, c*g*, c*h*, c*i*), 24.339 (c*f**, c*g**, c*h**, c*i**).

RESULTS AND DISCUSSION

Electronic Spectra

The absorption spectra of both perylene dyes show the characteristic vibronic structure associated with the π→π* transitions of perylene diimides between 450–524 nm (Fig. 2). A concentration dependent broad band at

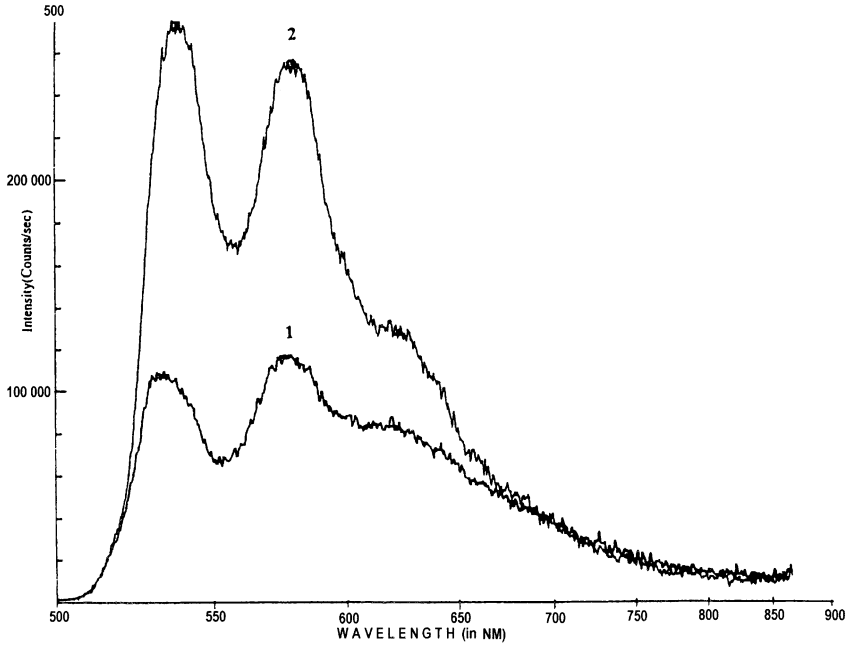


Figure 2. UV-VIS absorption spectrum of **1** (–) and **2** (----) in N,N-dimethylformamide.

600 nm, probably due to aggregation in solution was observed on the UV spectrum of N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) **(1)**. The broad band was dissapeared after filtration of the solution with microfilter (SPR 25 0,2 μm).The extinction coefficients (ε) obtained from the absorbance vs. concentration measurements in N,N-dimethylformamide are shown in Table 1. Small variation on extinction coefficients may be attributed to inductive effect of the p-hydroxy group in **1** and changes of the dihedral angle of the C-N bond which is expected to be larger in **2** due to steric hindrance.

The fluorescence spectra at the excitation wavelength of 485 nm of dye **1** and **2** are shown in Fig. 1. The emission spectrum of N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) **(1)** shows three bands at 533.9, 577.8, and 620.8 nm from singlet excited states. The emission spectrum of N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) **(2)** shows similar bands at 537.6, 577.9, and 622 nm. No excimer emission was observed in fluorescence spectra. Both dyes show weak fluorescence, possibly due to aggregation in solution. The fluorescence quantum

Table 1. Visible Absorption Maxima (λ_{max}) and Extinction Coefficients (ε) of **1** and **2** Measured in N,N-dimethylformamide at Room Temperature

Compound	λ_{max}/nm	ε/l mol^{-1} cm^{-1}
1	454	14430
	486	28490
	522	40240
2	458	13380
	488	35340
	524	55390

yields of **1** and **2** were determined by using perylene 3,4,9,10-tetracarboxylic acid-bis-N,N′-dodecyl diimide as reference ($\phi_f = 1.0$). The experiments with **1** and **2** give the quantum yields $\phi_f = 0.054$ and $\phi_f = 0.110$, respectively.

Infrared Spectra

The infrared spectrum of N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Peryenebis (dicarboximide) **(1)** shows O-H stretch at 3432 cm^{-1}, aromatic C-H

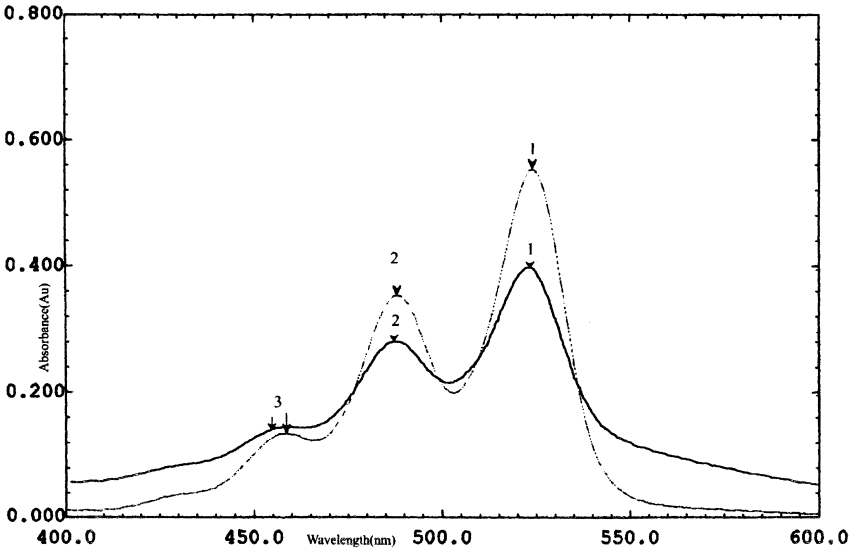


Figure 3. Fluorescence emission spectra of **1** and **2** in N,N-dimethylformamide.

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stretch at 2931 cm^{-1}, C=O stretch at 1639 and 1559 cm^{-1}, out-of-plane C-H bend at 809 cm^{-1}, Out-of-plane O-H bend at 643 cm^{-1}. The infrared spectrum of N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) **(2)** shows N-H stretch at 3449 cm^{-1}, C-H stretch at 2971 cm^{-1}, imide C=O stretch at 1690, 1651, 1595, and 1577 cm^{-1}, out-of-plane C-H bend at 745 and 809 cm^{-1}.

Stability

The chemical and photochemical stabilities of **1**, and **2** are very high. Stock solutions are stable when exposed to light months at room temperature. The quantum yields in nitrogen saturated solvents and in normal solvent are equal. Dye **2** is easily prepared. It is used as an electron acceptor in a photochemical reaction which the results of these investigation will be reported elsewhere. The acetonitrile, water solution is used as solvent. The electron transfer reaction, which is taken in flatbed reactors, is completed in one month at room temperature under sunlight at nitrogen atmosphere. After the addition of distilled water into mixture all the dye has passed into water layer. We obtained the dye **2** with water extraction easily. No decomposition is detected on the sample. So it is reusable.

Water Solubility

Solubility of dye **1** and **2** were measured as 4.4×10^{-5} g/ml and 5.0×10^{-3} g/ml respectively in distilled water at pH: 7. The solubility of **2** was increased with decreasing pH.

CONCLUSIONS

Two different perylene derivatives, N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) and N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) have been synthesized. Both of them dissolve in water and show high thermal and photochemical stability. N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) is much more soluble comparing to N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide). N,N′bis(4-Hydroxyphenyl)-3,4,9,10 Perylenebis (dicarboximide) can be obtained in pure grade with column chromatography in small amounts. It is not convenient for many applications for this reason. N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) has been obtained via a short and

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efficient synthetic pathway in large amounts without column chromatography. With water extractions the dye can be separated easily from organic solutions, it is also reusable. It does not decompose after one-month irradiation under sunlight. Thermally it is also very stable. With this unique set of properties N,N′bis(3,3,5,5-tetramethyl piperidine)-3,4,9,10-Perylenebis (dicarboximide) is offered as photosensitizers for photoenergy transfer and electron transfer reactions occurred in water. It is a very convenient standard for fluorescence quantum yield measurements in water. Also it is potential candidates for fluorescence labelling and immunofluorescence technique in biochemical analyses.

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