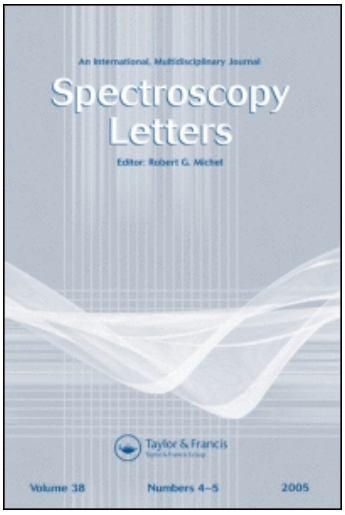

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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF HIGHLY PURE PERYLENE FLUORESCENT DYES

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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF HIGHLY PURE PERYLENE FLUORESCENT DYES

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ABSTRACT

Two new perylene dye, N,N′-bis-(aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)** and N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis (dicarboximide) have been synthesized. Because the solubility of perylene derivatives is very low, their synthesis and purification are difficult. The imides **1** and **2** are easily prepared with high yield. Dye **2** has a lower density than the density of air. They are highly fluorescent and very photostable dyes. With high fluorescent quantum yield they are suggested as new convenient standards for the fluorescence quantum yield measurements in 500–650 nm region. The report includes the electronic absorption and emission spectra, extinction coefficients and fluorescence quantum yields. Applications of the dyes are discussed.

Key Words: Fluorescent probes; Perylene dye; Fluorescent quantum yield; Photosensitizer.

*Corresponding author.

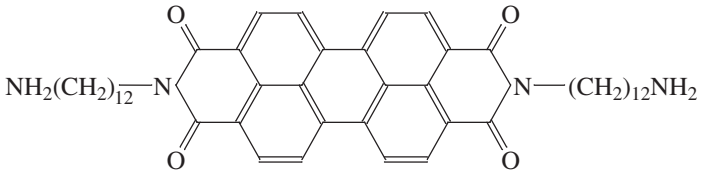
INTRODUCTION

The perylene dyes exhibit high fluorescence quantum yields, high photostability and thermal stability (higher than 550°C) and chemical inertness. The solubility of the dyes and other properties can be controlled with the substituents at the nitrogen atoms (1,2). They have been used widely in reprographic processes, solar cells, photovoltaic devices and dye lasers (3). They are strongly searched for design and preparation of molecular opto-electronic devices (3), for the fluorescence -labelling of liposomes (4), for camouflage materials (5), for electron transfer reactions as electron acceptor (6) . Bathochromic shift is related to the electronic interaction of the π-systems (7). The oxidation and reduction potentials are strongly effected with extension of the aromatic core between the imide groups (8). The low solubility of perylenes cause problem in synthesis, purification and spectroscopic investigations. Also the possible aggregation in solutions reduce the fluorescent quantum yields dramatically. It is therefore of prime interest to obtain easily prepared perylene dyes with high fluorescent quantum yields.

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



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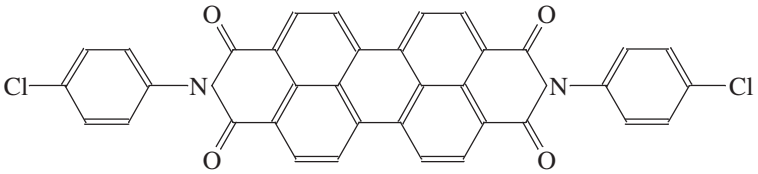

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Figure 1. Structural formulae of N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis(dicarboximide) **(1)** and N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis(dicarboximide) **(2)**.

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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%, 1,12-diaminododecane, 98%, and 4-chloroaniline, 98% were obtained from Aldrich. All solvents used for column chromatography were distilled before use.

Synthesis

Since the synthetic procedures of perylene dye **1** and **2** are all similar, only **1** is given as a representative example. N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)**: A mixture of perylene-3,4,9,10-tetracarboxylic acid dianhydride (1g, 2.55×10^{-3} mol), 1,12-diaminododecane (10.2 g, 50.9×10^{-3}), m-cresol (40 ml) and isoquinoline (4 ml) was stirred at 50°C for 2 hour. Then the solution was heated at 130°C for 5 hours, the temperature was raised to 150°C and kept for 4 hours. The reaction was then completed by stirring at 200°C for another 3 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 2% NaOH until the characteristic green fluorescent colour of perylene dianhydride disappear and then treated with ethanol in a Soxhlet apparatus for 24 hours, in order to get rid of the unreacted 1,12-diaminododecane and high boiling point solvents, m-cresol and isoquinoline.

Characterization

N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)**: Yield: 1.9 g (98%), color: black, m.p > 360°C. IR: ν (KBr pellets)/ cm^{-1} 3422, 2923, 2851, 1695, 1655, 1594, 1578, 1506, 1465, 1439, 1403, 1343, 1246, 1158, 1089, 853, 809, 746, 630, 435 cm^{-1}. UV-VIS: λmax ($CHCl_3$)/nm (ε/mol^{-1} cm^{-1}) 457.80 (6500), 489.40 (17875), 525.40 (28500). Fluorescence: λ_{max} ($CHCl_3$)/nm 535.95, 577.74, 624.05. Qf = 0.83. MS: m/z: 757.4 (M+1), 398.2, 341.1, 290.2, 267.2, 201.2. ^{1}H NMR: δ_H (250 MHz, $CCl_3D + C_2DF_3O_2$, 5:3): 1.2-1.4 (aliphatic C-H), 4.20(CH_2-N), 8.7 (Ar-H). ^{13}C NMR: δ_C (252 MHz, $CCl_3D + C_2DF_3O_2$, 5:3): δ: 162.774 (CO), 162.081 (CO), 120.872, 116.357, 111.838, 107,322 (Ar-C). C_{48} H_{60} N_4 O_4: Calcd. C 76.16, H 7.99, N 7.40; found C 75.99, H 7.88, N 7.28.

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N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis(dicarboximide) **(2)**:Yield: 1.54 g (98.7 %), color of the diimide: velvet-red, m.p > 360°C, IR: ν (KBr pellets)/ cm^{-1} 3126, 1705, 1671, 1592, 1492, 1403, 1357, 1344, 1256, 1177, 1088, 860, 839, 828.809, 793, 745. UV-VIS: λ_{max} (DMF)/nm (ε/mol^{-1} cm^{-1}) 458.20 (30940), 488.60 (54630), 524.40 (75130). Fluorescence: λ_{max} (DMF)/nm 538.59, 579.85, 625.56. Q_f: 0.84. MS: m/z 611 (M+ 1), 537.6, 381.2, 314.0, 245.0, 172.0, 129.6. ^{13}C NMR: δ_C (252 MHz, CCl_3D + $C_2DF_3O_2$, 5:3): δ: 162.503 (CO), 161.812 (CO), 144.897, 136.705, 120.906, 116.387, 111.869, 107,352 (Ar-C). C_{36} H_{16} N_2 O_4 C_{12}: Calcd C 70.72, H 2.64, N 4.58, Cl 11.60; found C 70.86, H 2.63, N 4.52, Cl 11.46

RESULTS AND DISCUSSION

Electronic Spectra

The UV-vis and fluorescence spectra of **1** and **2** are shown in Figures 2 through 5. Both of the dyes show three characteristic absorption bands between 450–525 nm. Molar extinction coefficients are reported in Table 1. No tendency to aggregate in solution is observed. The fluorescence spectra show the expected

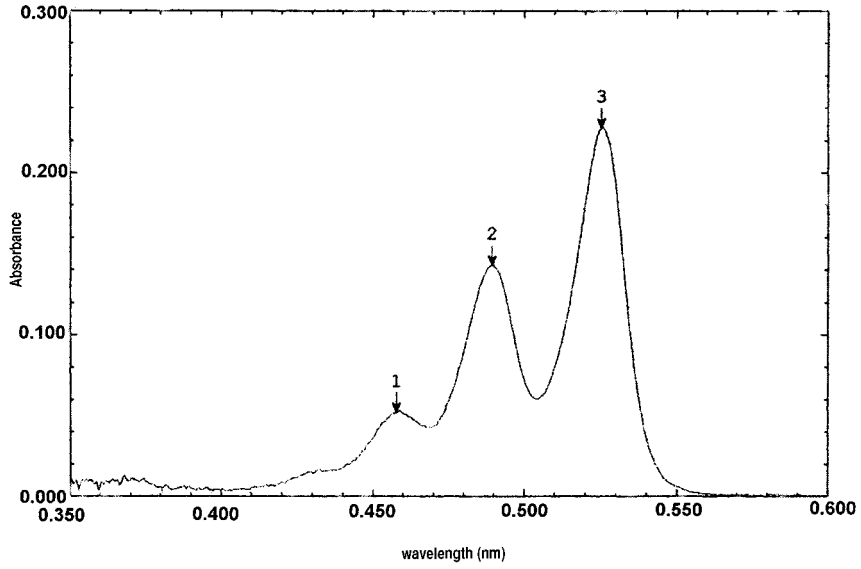

Figure 2. Absorbance spectrum of N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)** in chloroform.

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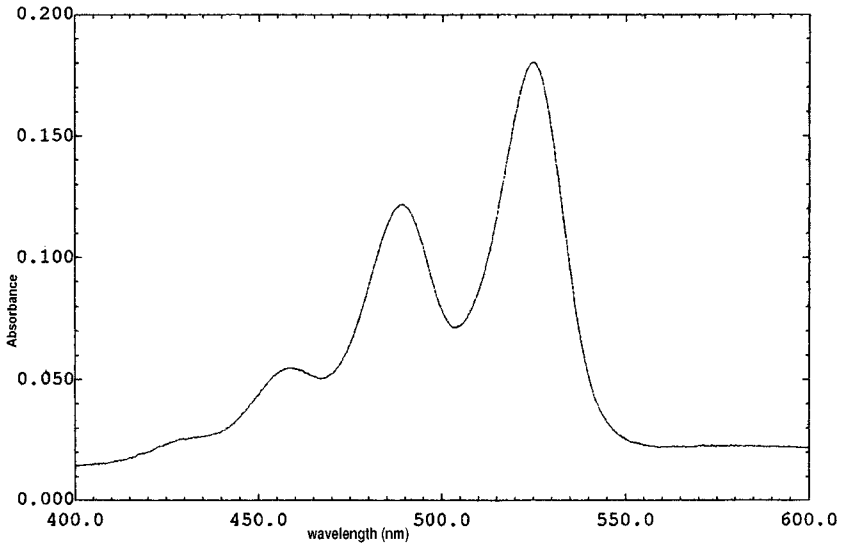

Figure 3. Absorbance spectrum of N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis (dicarboximide) **(2)** in N,N-dimethylformamide.

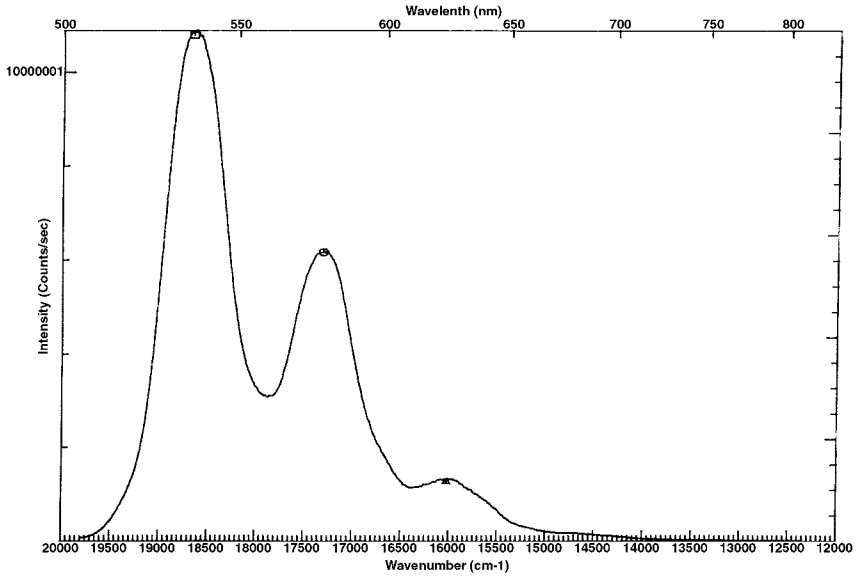

Figure 4. Fluorescence emission ($\lambda_{exc} = 485$ nm) spectrum of N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)** in chloroform.

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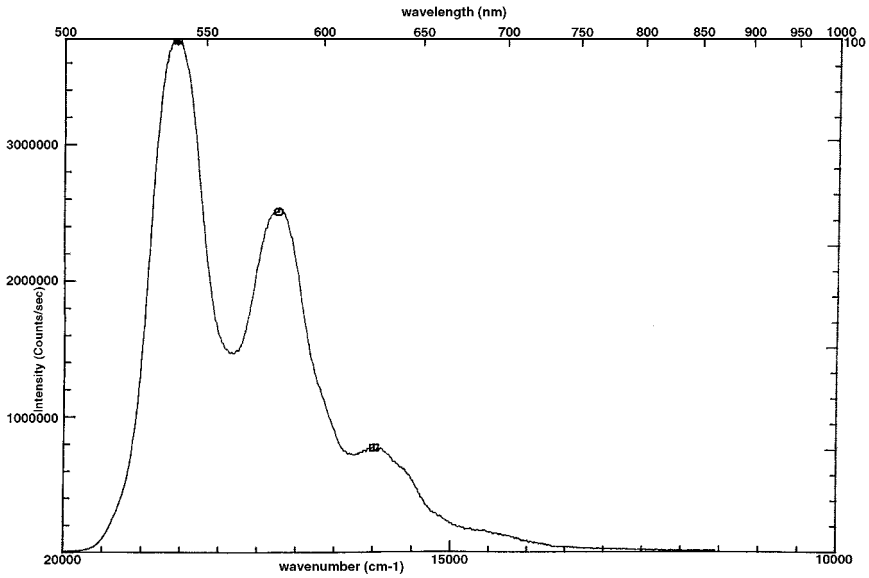

Figure 5. Fluorescence emission ($\lambda_{exc} = 485$ nm) spectrum of N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis (dicarboximide) **(2)** in N,N-dimethylformamide.

mirror-image symmetry with the absorption spectra. Dyes **1** and **2** are highly fluorescent. No excimer emission is observed in the fluorescence spectra. The fluorescence quantum yields of **1** and **2** are determined by using perylene 3,4,9,10-tetracarboxylic acid-bis-N,N′-dodecyl diimide as a reference ($\phi_{f(\mathbf{REF})} = 1.0$, $\phi_{f(\mathbf{1})} = 0.83$, $\phi_{f(\mathbf{2})} = 0.84$). The absorption and emission bands are not influenced by

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

Compound	λ_{max}/nm	ε/1 mol^{-1} cm^{-1}
1	457.8	6500
	489.4	17875
	525.4	28500
2	458.2	30940
	488.6	54630
	524.4	75130

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the type of substituents, but the extinction coefficients, stability and aggregation are strongly dependent on the N-substitution.

Infrared Spectra

The infrared spectrum of N, N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)** exhibits N-H stretch at 3422 cm^{-1}, aliphatic C-H stretch at 2923 and 2851 cm^{-1}, C = O stretch at 1695, 1655 and 1594 cm^{-1}, out-of-plane C-H bend at 809 and 746 cm^{-1}. C-N stretch at 1343 cm^{-1}. The infrared spectrum of N,N'-bis-(4-chlorophenyl)-3,4,9,10-perylenebis (dicarboximide) **(2)** exhibits aromatic C-H stretch at 3126 cm^{-1}, C = O stretch at 1705, 1671 and 1592 cm^{-1}, aromatic C-Cl stretch at 1088 cm^{-1} , out-of-plane C-H bend at 809, 793 and 745 cm^{-1}. The infrared spectra of **(1)** and **(2)** are shown in Figures 6 and 7, respectively.

Stability

Dyes **1** and **2** show high chemical and photochemical stability. The compounds are not quenched with oxygen. They act as electron acceptor even in heterogeneous phase which the results of these investigations will be reported elsewhere. In the argon atmosphere they do not decompose even after one month irradiation with sunlight.

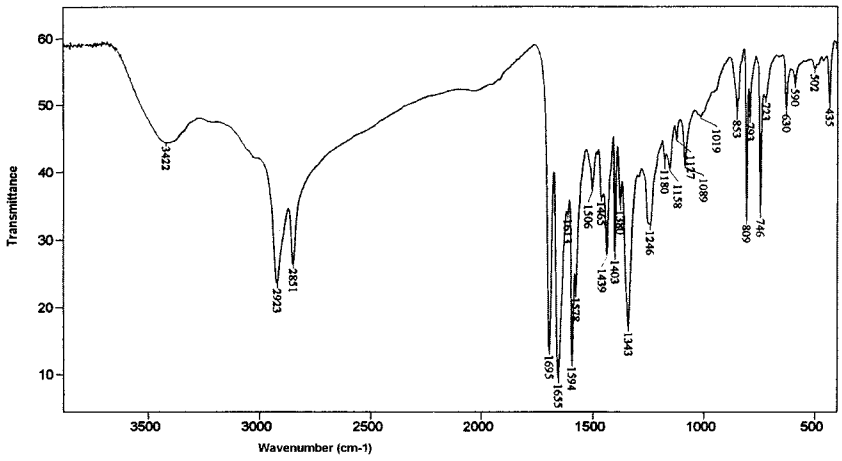

Figure 6. IR spectrum of N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)**.

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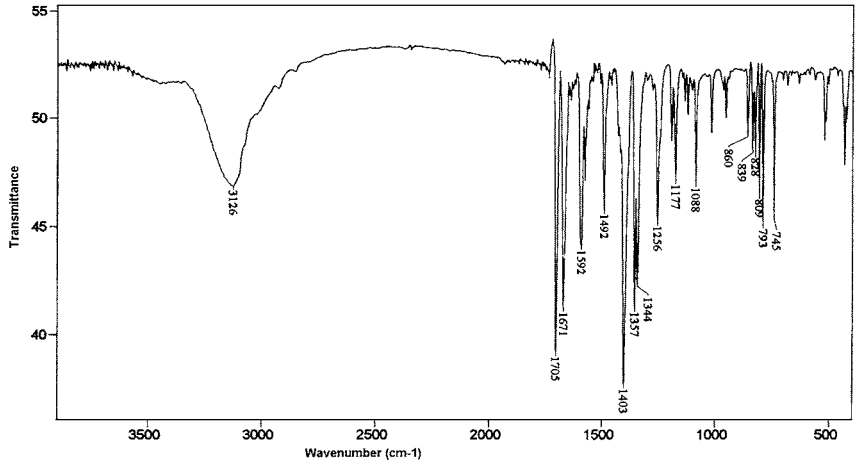

Figure 7. IR spectrum of N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis (dicarboximide) **(2)**.

CONCLUSION

In the present study two new perylene dyes, N,N′-bis-(12-aminododecyl)-3,4,9,10-perylenebis (dicarboximide) **(1)** and N,N′-bis-(4-chlorophenyl)-3,4,9,10-perylenebis(dicarboximide) **(2)** are synthesized with high yield and purity via a very simple and effective synthetic pathway. Many of the perylene dyes published within the literature have been obtained in pure grade only by using column chromatography; thus they are not useful for various applications. Chemical and photostability of all perylene dyes are not identical. Dyes **1** and **2** show excellent chemical and photochemical stability. The density of dye **2** is lower than the density of air. With its density **2** is very different from the other perylene dyes. The compounds are very fluorescent in solution ($\phi_{f(\mathbf{1})} = 0.83$ and $\phi_{f(\mathbf{2})} = 0.84$). They can be good sensitizers for energy transfer and electron transfer reactions occurring through the singlet energy state. They are very convenient standards for fluorescence quantum yield measurements.

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