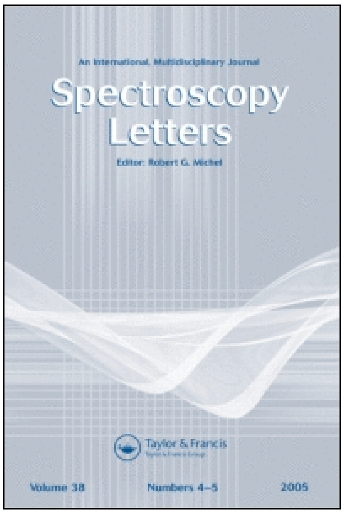


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Synthesis and Properties of a New Photostable *Soluble Perylene Dye*: N,N'-Di-(1-Dehydroabietyl) Perylene-3,4,9,10-Bis(Dicarboximide)

Huriye Ice[a]; Siddik Icli[b]; Çiğm Sayil[c]
[a] Department of Chemistry, Faculty of Arts and Science, Eastern Mediterranean University, Mersin, Turkey [b] Department of Chemistry, Faculty of Science, Ege University, Izmir, Turkey [c] TUBITAK-Marmara Research Center, Research Institute for Basic Sciences, Department of Chemistry, Turkey

**To cite this Article** Ice, Huriye , Icli, Siddik and Sayil, Çiğm(1998) 'Synthesis and Properties of a New Photostable *Soluble Perylene Dye*: N,N'-Di-(1-Dehydroabietyl) Perylene-3,4,9,10-Bis(Dicarboximide)', Spectroscopy Letters, 31: 8, 1643 — 1647

**To link to this Article: DOI:** 10.1080/00387019808007441

**URL:** http://dx.doi.org/10.1080/00387019808007441

SPECTROSCOPY LETTERS, 31(8), 1643-1647 (1998)

# SYNTHESIS AND PROPERTIES OF A NEW PHOTOSTABLE *SOLUBLE PERYLENE DYE* :N,N'-DI-(1-DEHYDROABIETYL) PERYLENE-3,4,9,10-BIS(DICARBOXIMIDE)

HURIYE ICIL [#,*],SIDDIK ICLI [Y] AND ÇIĞDEM SAYIL [δ]

[#]Department of Chemistry, Faculty of Arts and Science, Eastern Mediterranean University, Famagusta, N.Cyprus, Mersin 10,Turkey

[Y]Department of Chemistry, Faculty of Science, Ege University, 35100 Bornova, Izmir, Turkey

[δ]TUBITAK-Marmara Research Center, Research Institute for Basic Sciences, Department of Chemistry, P.O.Box 21, 41470 Gebze-Kocaeli/Turkey

**Abstract** – N,N'- Di-(-1-Dehydroabietyl) perylene -3,4,9,10-bis(dicarboximide) is prepared in 95 % yield by the condensation of perylene 3,4,9,10-tetracarboxylic dianhydride with dehydroabietyl amine. Thermal and photostable bright red-orange dye is measured to have a fluorescence quantum yield of unity, $Q_f = 1$, in chloroform solutions. Solubility of the dye is 1.8 g/L in chloroform.The diimide is an ideal reference probe for fluorescence quantum yield measurements in 500-650 nm region and also very interesting dye for chemiluminescent light devices.

## INTRODUCTION

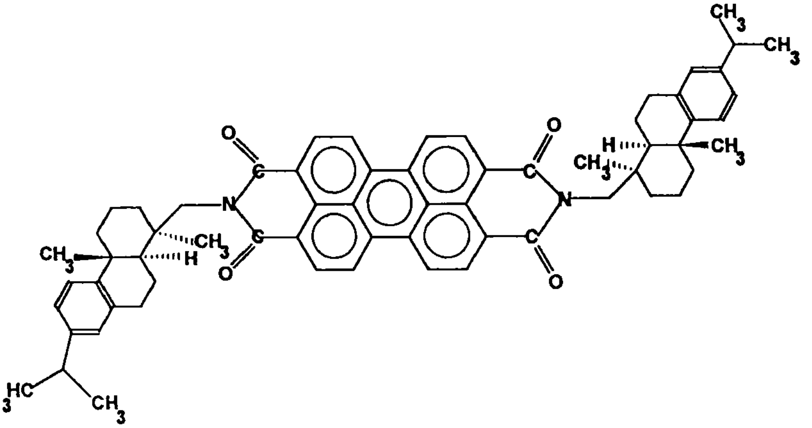
Brilliant, red, technical pigments, perylene 3,4,9,10-tetracarboxylic bisimides have been discovered by Kardos in 1913[3]. Due to their low solubility however their high fluorescent potential could not be discovered until 1959. Nearly all perylene dyes are thermally and photochemically very stable[1].The photostability and solubility depend strongly on the substituents.To obtain readily soluble perylene dyes are very important in respect to use their strong fluorescence capacity. Generally bulky aliphatic substutients enhance the solubility[4].

---

*Author to whom correspondence should be address.

The fluorescence quantum yield is about unity for the most derivatives[1]. The soluble perylene diimides can be used as light emitting species in oxalate chemiluminescent devices[2] due to their chemical stability.The uv/vis spectrum of these dyes depend weakly to the substituents. Recently perylene diimides are used as sensitizing dye in semiconductor systems[5]. H.Langhals and J.Gold have shown that trichromophoric perylene dyes show an unusually large bathochromic shift due to minimizing the steric and through-bond interactions of the chromophores[6].M.Lan.et.al have investigated the photoelectric behaviour of mixtures of 3,4,9,10-perylenetetracarboxylic diimides (PTCDI) and AmZnPc by the Langmuir-Blodgett film technique.[7]We have synthesized recently the first perylene polymer in the literature. The polymer is three times more thermally stable than all the perylene dyes[1].

We report here a very soluble (1.8 g/L, chloroform) perylene 3,4,9,10-tetracarboxylic bisimide which we offer it as an excellent reference probe for fluorescence quantum yield measurements in 500-650 nm region , as light emitting species in oxalate chemiluminescent light devices and furthermore a sensitizer in photovoltaic devices.



## EXPERIMENTAL

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (1 g, 2.55 x $10^{-3}$ mol), dehydroabietylamine (1.456 g, 5.1 x $10^{-3}$ mol), m-cresol (40 ml) and isoquinoline (4 ml) are heated 1 hour at 80 °C, 2 hour at 120 °C, 2 hour at 160 °C and 4 hour at 200 °C. The warm solution is poured in 500 mL of acetone. The orange-red solid is collected by vacuum filtration, dried in vacuum oven at 120 °C. The crude product is treated with acetone in a Soxhlet apparatus for 24 hour, in order to remove high boiling solvents, m-cresol and isoquinoline. The pruduct is dissolved in chloroform and poured in 250 mL of acetone. The precipitate is collected by vacuum filtration and dried in vacuum oven at 120 °C. 2.27 g (96%) pure product is obtained. m.p.> 300 °C. - UV($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 458 nm (25800), 490 nm (58950), 526 nm (93200). - Fluorescence ($CHCl_3$): $\lambda_{max}(\varepsilon)$ =

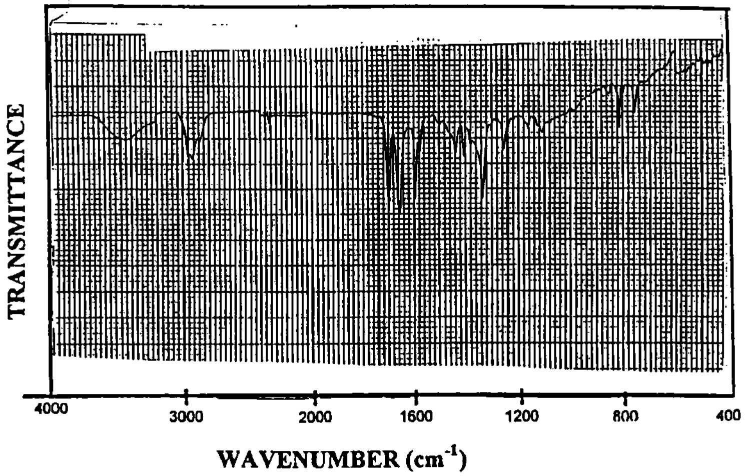


**Figure 1 : IR spectrum of N,N'- Di-(-1-Dehydroabietyl) perylene -3,4,9,10-bis(dicarboximide)**

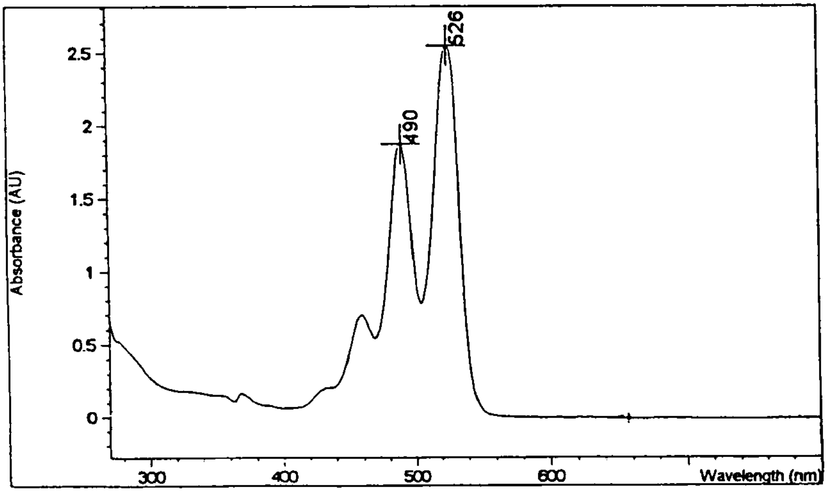


**Figure 2 : Absorbance spectrum of N,N'- Di-(-1-Dehydroabietyl) perylene -3,4,9,10-bis(dicarboximide) in chloroform.**

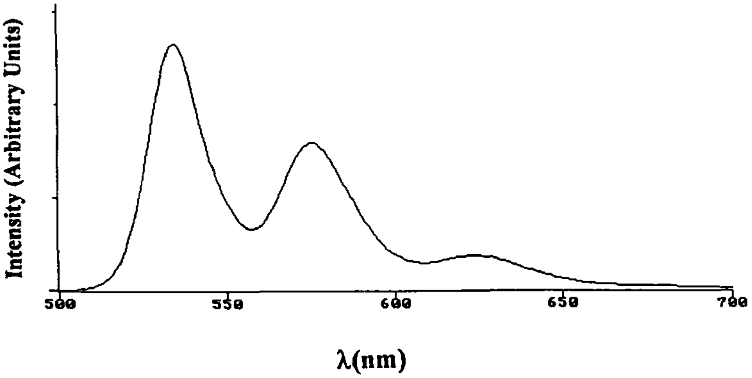


**Figure 3 : Fluorescence ($\lambda_{exc}$ = 485 nm) spectrum of N,N'- Di-(-1-Dehydroabietyl) perylene -3,4,9,10-bis(dicarboximide) in chloroform.**

536 nm, 577 nm, 625 nm. – IR (KBr): $\nu$ = 2920 $cm^{-1}$($CH_3$), 1699 $cm^{-1}$ and 1658 $cm^{-1}$ (imide carbonyl), 1598 $cm^{-1}$, 1440 $cm^{-1}$,1400 $cm^{-1}$, 1340 $cm^{-1}$,1250 $cm^{-1}$, 810 $cm^{-1}$, 755 $cm^{-1}$. - $^1$H NMR ($CDCl_3$): $\delta$ = 8.3 (8H), 7.2 (2H), 7.1 (2H), 7.0 (2H), 4.1 (4H), 3.0 (2H ), 2.8 (12H ), 1.6 (12 H), 1.4 (20 H), 0.9 (2 H). - $^{13}$C NMR ($CDCl_3$): $\delta$ = 164.1 (C=O), 147.5 , 145.5, 135.0, 134.0, 131.2, 128.9, 126.9, 125.8, 123.9, 123.7, 123.2, 122.7, 50.1(CONCH$_2$-), 46.5, 40.0, 38.2, 37.8, 37.5, 33.5, 30.5, 26.0, 24.0, 19.9, 19.2, 18.9. MS (70 eV), m/z (%): 927.6 [$M^+$] (14), 725.3 (6), 659.3 (21), 404.1 (96), 321.1 (2.2). - $C_{64}H_{66}N_2O_4$ (927.3): calcd. C 82.9, H 7.17, N 3.02; found C 83.07, H 7.51, N 2.47.

Perylene-3,4,9,10-tetracarboxylic dianhydride, pure grade, dehydroabietylamine, technical grade, and isoquinoline, 97% were obtained from Aldrich. M-cresol, 98%, was supplied by Fluka, and used without further purification. Acetone and chloroform were purchased from Aldrich .

UV spectrophotometric measurements were carried out with a Hewlett-Packard HP 8452A diode array spectrophotometer. Emission spectra were measured on a Spex Fluorolog 2 spectrophotometer. IR spectra were recorded with Perkin-Elmer 983 IR spectrometer. Mass-GC chromatograms and spectra were recorded with Fisons GC MD800 quadrupole and Fisons MS VG Zabspec magnetic sector instrument combination. Proton nmr spectra were recorded with a Bruker AC 200 L 200 MHz NMR spectrometer. Carbon-13 nmr spectra were obtained at 300 MHz on a QE-300 GE-Nicolet spectrometer. Spectra are shown in Figures 1,2,3.

## RESULTS AND DISCUSSION

The UV spectrum of the diimide shows typically three absorption bands at 458-526 nm for the highest occupied bonding energy levels. Characteristic imide absorptions on

IR were observed. The molecular peak is detected at 927.6 m/e. Proton nmr spectrum in $CDCl_3$ is, δ ppm: methyl (0.9), $CH_2$-N (4.1), Ar-H (8.1-7.2), Ar-$CH(CH_3)_2$ (3.0, 2.8), remaining methylene protons are observed as multiplets at 1.4-1.6 ppm.

The solubility is so high, 1.8 g/L in chloroform with brilliant red-orange fluorescent color. The emission spectrum at an excitation wavelength of 485 nm shows three bands at 536, 577, and 625 nm from singlet excited states. No excimer emission was observed. The fluorescence quantum yield is measured as 1.00 in reference to the rhodamine 101 , in chloroform at emission spectrum of $\lambda_{exc}$= 485 nm.

The highly soluble perylene diimide will be mostly useful as light emitting species in oxalate chemiluminescent light devices and for photovoltaic devices. Moreover it is a perfect reference probe for fluorescence quantum yield mesurements and exciting photosensitizer for solar photochemical applications.

## ACKNOWLEDGEMENTS

The authors wish to express their gratitude to TUBITAK and NATO for their research support and also to Prof.Dr.D.Whitten at Rochester University for providing facilities of spectral analyses.

## REFERENCES

1. Icil H., Içli S.,"*Synthesis and properties of a new photostable polymer: perylene-3,4,9,10-tetracarboxylic acid-bis-N,N'-dodecylpolyimide.*" **J. Polym. Sci. A:Polym Chem** (1997) **35**, 2137-2142.
2. C.Dugliss, E.P. 201704 , Chem Abstr., 1987, 106, 93364s.
3. Heinz Langhals, "*Cyclic carboxylic imide structures as structure elements of high stability. Novel developments in perylene dye chemistry.*" **Heterocycles** (1995) **40(1)**, 477-500.
4. H. Langhals, St. Demmig, Th. Potrawa, "*The relation between Packing Effects and Solid State Fluorescence of Dyes*" **J. F. Prakt. Chemie** (1991) **333(5)**, 733-748.
5. Suzanne Ferrere, Arie Zaban, and Brian A. Gregg, "*Dye sensitization of nanocrystalline tin oxide by perylene derivatives*" **J. Phys. Chem** (in press)
6. H.Langhals, and J.Gold, "*Tangentially Coupled π Systems and Their Through-Space Interaction-Trichromophoric Perylene Dyes*" **J.prakt.Chem.** (1996), 338, 654-659.
7. M.Lan, S.Ren, J.Jia, X.Xiao, "Photoelectric Conversion of a Novel Langmuir-Blodgett Film" **Dyes and Pigments** (1997), 33, 79-86.

Date Received: May 11, 1998
Date Accepted: June 18, 1998