

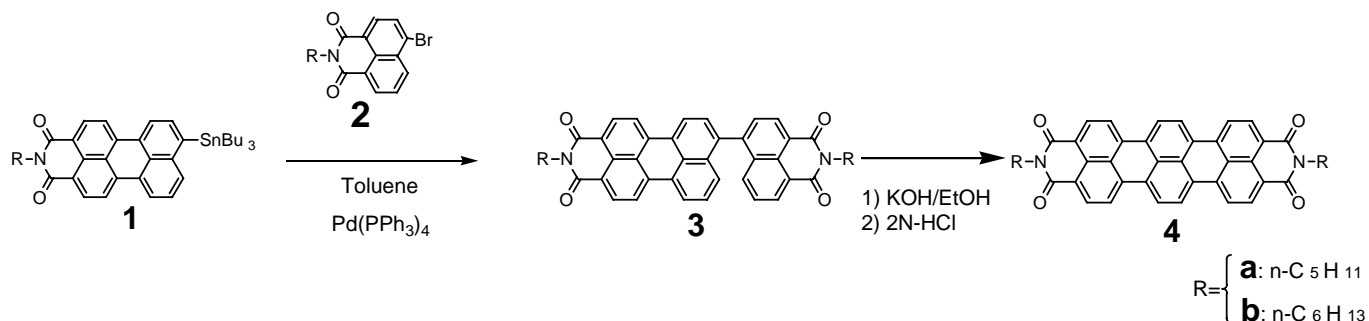
SYNTHESIS AND PROPERTIES OF TERRYLENE-DICARBOXIMIDE DERIVATIVES[≠]

Yukinori Nagao,* Hironobu Iwawaki, and Kozo Kozawa

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

Abstract - Terrylenedicarboximide derivatives were prepared by the coupling of *N*-alkyl-9-tributylstannylperylene-3,4-dicarboximides with 4-bromo-1,8-naphthalimide derivative and the following ring closure reaction. Spectral properties in solution or in the solid state and the thermal stability of these derivatives were investigated.

Near-infrared (NIR) absorbing materials have been used as charge-generation materials and the fluorescent dyes have been used as organic electroluminescence devices.¹ These materials are noticed in the area from electronic to biological fields. For practical application, stabilities (light, heat, etc.) are generally required.^{2,3}



Scheme 1

[≠] Dedicated to the memory of the departed Professor James P. Kutney.

Previously the preparation of many perylene derivatives has been investigated and the terrylene derivatives are expected to have middle properties between those of perylene and quaterrylene.⁴⁻¹⁰

In this paper, the synthesis of terrylenedicarboximide derivatives is described (Scheme1). The absorption spectra of in solution in solid state, the fluorescence spectra, and the thermal stability of these derivatives are also reported.

Preparation of naphthylperylene derivatives (**3a, b**) and terrylenedicarboximide derivatives (**4a, b**). Yield and spectral data of the naphthylperylene derivatives (**3a,b**) prepared by the coupling reaction of *N*-alkyl-9-tributylstannylperylene-3,4-dicarboximides(**1a,b**) with 4-bromo-1,8-naphthalimide derivative(**2a,b**) are listed in Table 1. Compounds (**3a,b**) were obtained in good yield. The IR spectra of these compounds showed imide $\nu_{C=O}$ at 1686-1688 cm^{-1} and 1648-1652 cm^{-1} . The molecular ion peak of these compounds could be detected and these compounds were characterized by these spectral data and $^1\text{H-NMR}$ spectroscopy.

Table 1 Yield and spectral data of 3a,b^{a)}

Compd	R	Yield (%)	IR ^{b)} Imide $\nu_{C=O}(\text{cm}^{-1})$	UV-VIS (nm)		MS (m/z)
				$\nu_{\text{max}}^{\text{c)}$	$\nu_{\text{max}}^{\text{d)}$	
3a	n-C ₅ H ₁₁	76.4	1687, 1649	626	510,483	656(M ⁺)
3b	n-C ₆ H ₁₃	75.0	1688, 1652	625	510,483	684(M ⁺)

a) React. temp.: reflux(110 °C). React. time:96 h. Molar ratio: 1:2 = 1:1 .

b) KBr disk method. c) Solv.: conc. H₂SO₄(95%). d) Solv.: CHCl₃.

Yield and spectral data of terrylenedicarboximides (**4a,b**) prepared by the ring closure reaction of **3a,b** with potassium hydroxide in ethanol are listed in Table 2. Compounds (**4a,b**) were obtained in high yields. The IR spectra of these compounds showed imide $\nu_{C=O}$ at 1686-1688 cm^{-1} and 1648-1652 cm^{-1} . The molecular ion peak of compounds (**4a,b**) could be detected on MS.

Table 2 Yields and spectral data of **4a,b** ^{a)}

Compd	R	Yield (%)	IRb) Imide $\nu_{C=O}$ (cm^{-1})	VIS-NIR (nm)		MS (m/z)
				$\lambda_{\text{max}}^{\text{c)}$	$\lambda_{\text{max}}^{\text{d)}$	
4a	n-C ₅ H ₁₁	93.0	1688, 1652	807	650	654(M ⁺)
4b	n-C ₆ H ₁₃	90.0	1687, 1651	807	650	682(M ⁺)

a) React. temp.: reflux (110 °C). React. time: 4 h.

b) KBr disk method. c) Solv.: conc. H₂SO₄. d) Solv.: CHCl₃.

In VIS-NIR absorption spectra in conc. H₂SO₄, compounds (**4a,b**) showed red shift of 182 nm compared to **3a,b** (625 nm).

Properties of terrylenedicarboximides (**4a,b**). The properties of absorption or fluorescence spectra and thermal stability for these terrylenedicarboximides derivatives were investigated. In absorption spectra in CHCl₃, the absorption curves of **4b** and perylenebis(dicarboximide) were very similar and the absorption maximum of **4b** (λ_{max} : 650 nm) was longer than that of perylenebis(dicarboximide) (λ_{max} : 525 nm). In addition, the molar absorption coefficient of **4b** (ϵ : 49000) was twice of that of perylenebis(dicarboximide) (ϵ : 24000).

Table 3 summarizes the observed and calculated absorption spectra of terrylenebis(dicarboximide) and perylenebis(dicarboximide). The calculated absorption spectra were obtained by the PPP method.¹¹ The observed λ_{max} of terrylenebis(dicarboximide) was 650 nm and that of perylenebis(dicarboximide) was 525 nm, but the calculated was 619 nm (terrylenebis(dicarboximide)) and 503 nm (perylenebis(dicarboximide)). The each dyes have similar discrepancy between the observed and calculated λ_{max} . This tendency was similar between terrylenebis(dicarboximide) and perylenebis(dicarboximide).

In fluorescence spectra of **4a** in CHCl₃, λ_{max} of excitation spectra was 650 nm and λ_{max} of emission spectra was 663 nm (Figure 2). The emission of terrylenebis(dicarboximide) (**4a,b**) was the same wavelength of the red light (Table 3). The shape of the emission spectrum in Figure 2 and that of absorption spectrum in Figure 1 was not a mirror image,

but the excitation spectrum was similar to absorption spectrum.

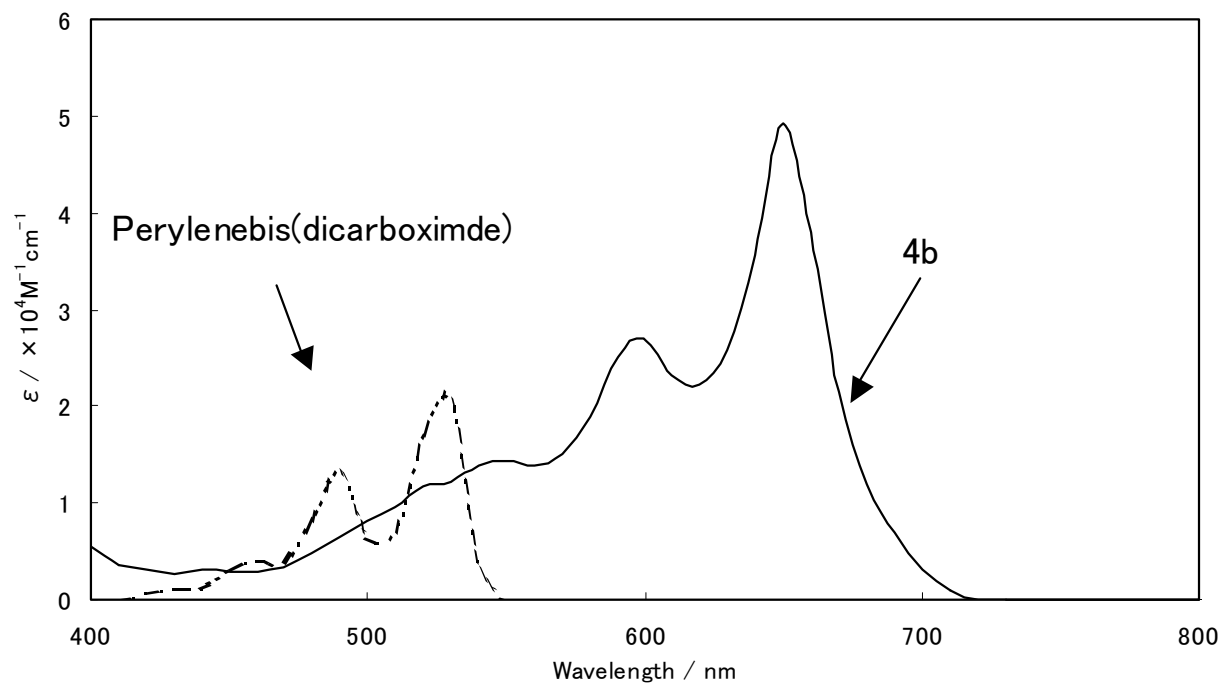
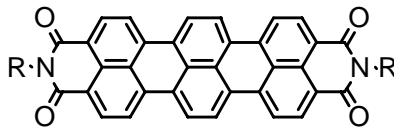
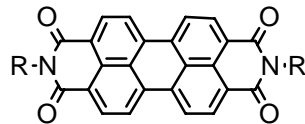


Figure 1 Visible absorption spectra of **4b** and perylenebis(dicarboximide) in CHCl_3

Table 3 Observed and calculated absorption spectra of **4b** and PTCAI

Dye	Observed	Calculated(PPP)	
	$\lambda_{\text{max}}^{\text{b)}$ (nm)	λ_{max} (nm)	$f^{\text{c)}$
 4	650 ^{a)}	619 ^{a)}	0.391 (HOMO,21-LUMO,22)
 PTCAI	525 ^{a)}	503 ^{a)}	1.289 (HOMO,16-LUMO,17)

a) Observed: R=n-C₆H₁₃, Calculated: R=CH₃

b) Solv.: CHCl₃

c) Oscillator strength

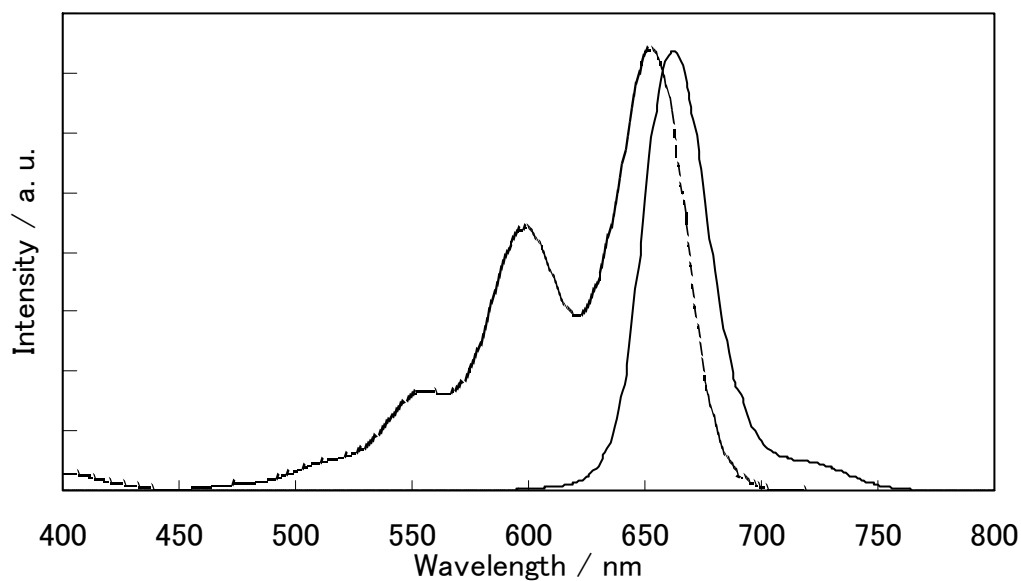
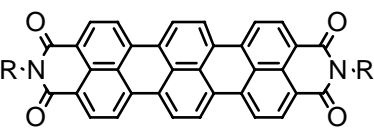
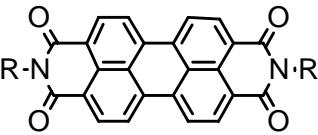


Figure 2 Excitation and emission spectra of **4a** in CHCl_3 ;
dashed line: excitation spectrum,
solid line: emission spectrum

Table 4 λ_{max} of absorption and emission spectra

Dye		Absorption ^{a)} λ_{max} (nm)	Emission ^{a)} λ_{max} (nm)
	4a	650 ($\epsilon : 4.9 \times 10^4$)	663
	4b	650 ($\epsilon : 4.8 \times 10^4$)	664
 R = n-C ₆ H ₁₃		525 ($\epsilon : 2.4 \times 10^4$)	532

a) Solv.: CHCl_3

In the absorption spectra in solid state for evaporated film and painted film, **4a,b** absorbed all visible range over 500 nm. Evaporated film of **4b** and perylenebis (dicarboximide), and painted film of **4a** gave a dark blue

transparent color.

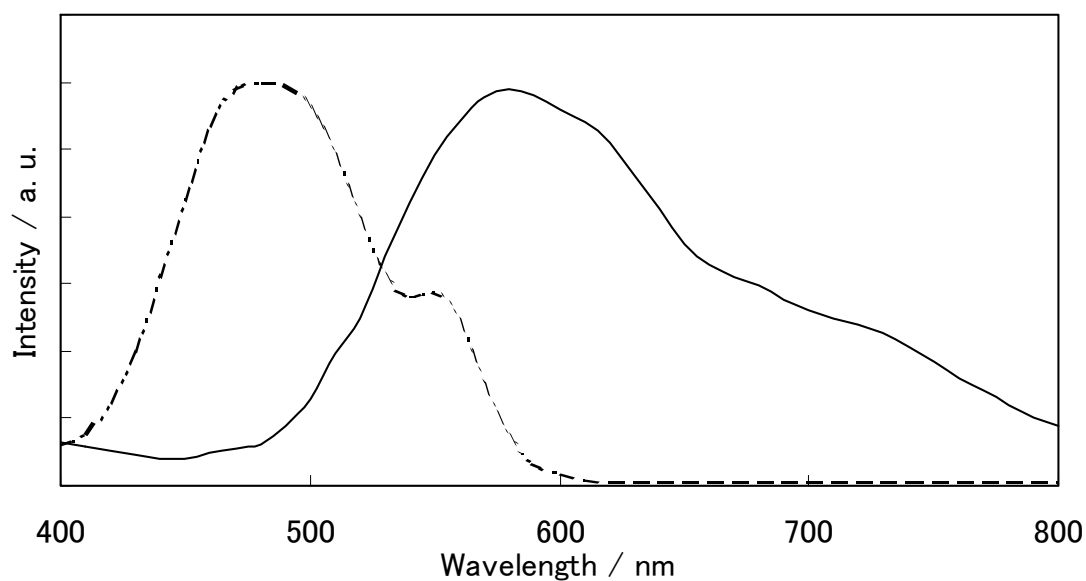


Figure 3 Visible absorption spectra of evaporated film of **4b** and perylenebis(dicarboximide); dashed line: perylenebis(dicarboximide), solid line: **4b**

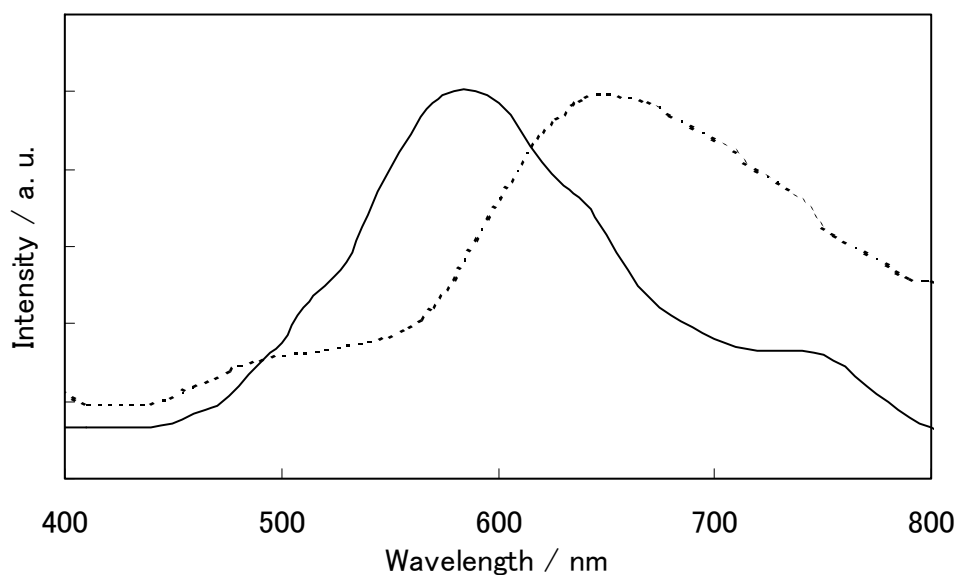
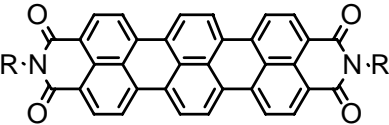
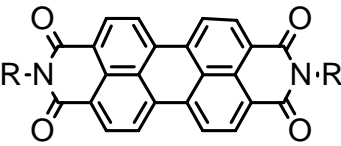


Figure 4 Visible absorption spectra of painted film of **4a**.

The thermogravimetry (TG) and differential thermal analysis (DTA) curves of the terylenebis(dicarboximide) derivatives (**4a, b**) showed similar two step decomposition curves and the thermal decomposition for **4a,b** by TG-DTA was shown at about 400 °C.

From DTA and TG curves, the first was due to the decomposition of alkyl chain and secondly was the decomposition of terylene skeleton. These dyes in Table 5 have the high stabilities for heat.

Table 5 Decomposition temperature of **4a,b** and perylenebis(dicarboximide)

Dye	Decomp. Temp. (°C)		
	Alkyl chain	Terylene skeleton	
	4a (R = n-C ₆ H ₁₃)	420	472
	4b (R = n-C ₆ H ₁₃)	387	471
	(R = n-C ₆ H ₁₃)	390	—

EXPERIMENTAL

3,4:9,10-Perylenetetracarboxylic dianhydride, all alkylamines, and 4-bromonaphthalic anhydride used were obtained commercially. *N*-Alkyl-4-bromonaphthalenedicarboximide (**2a,b**)(alkyl = pentyl and hexyl) were prepared by the condensation of 4-bromonaphthalic anhydride with alkylamines. *N*-Alkyl-9-bromoperylene dicarboximide (alkyl = pentyl and hexyl) were prepared as previously reported.⁶

MS spectra were recorded on a JEOL MStation JMS-700 mass spectrometer. Visible absorption spectra were recorded on a JASCO UVIDEK-610C and HITACHI 330, fluorescence spectra on a HITACHI F2500, IR spectra on a JASCO FT/IR-410 spectrophotometers. NMR spectra were measured on a JEOL JNM-AL300 and JEOL JNM-EX400 spectrometers (at room temperature). Thermal decomposition was measured with a MAC science WS002 differential thermal micro balance at a heating rate 10 °C min⁻¹ in air.

To form a thin film (evaporated film), vacuum deposition of the prepared pigments was carried out.

Paint film tests were carried out as follows: the prepared pigments (2.0 mg) and 2 mL of lacquer solution (contains 30 g of polymethylmethacrylate, 100 mL of tetrachloroethane and 30 g of butylbenzylphthalate) were mixed using muller and painted on transparent plastic film over a constant area (15 mm × 50 mm).

Tributylstannylperylene-dicarboximide derivatives (**1a,b**)

Tributylstannylperylene (**1a**) was prepared as follows. A solution of *N*-pentyl-9-bromoperylene-dicarboximide (1.00 g, 2.12 mmol), hexabutyl-ditin (1.85 g, 3.18 mmol), and Pd(PPh₃)₄ (0.012 g, 0.5 mol % of bromoperylene) in toluene (30 mL) was refluxed for 3 d. The solvent was evaporated and the residue purified by column chromatography (silica gel, CH₂Cl₂) and recrystallization from ethanol to give **1a** as a red solid (1.08 g, 75.2 %). **1b** was prepared in 65.5% yield from *N*-hexyl-9-bromoperylene-dicarboximide similarly.

1a, mp: 110.1-110.8 °C, IR (KBr disk method): ν = 1687, 1652 (C=O), ¹H-NMR (300 MHz, CDCl₃): δ = 0.82-0.88(m, 12H, -CH₃), 1.16-1.55(m, 22H, Sn-(CH₂)₃-, -(CH₂)₂-), 1.69(m, 2H, -CH₂-), 4.13(t, *J*=8 Hz, 2H, N-CH₂), 7.58(t, *J*=8 Hz, 1H, Arom.), 7.73(d, *J*=8 Hz, 1H, Arom.), 7.77(d, *J*=8 Hz, 1H, Arom.), 8.30(d, *J*=8 Hz, 1H, Arom.), 8.36(dd, *J*=8, 8 Hz, 2H, Arom.), 8.40(d, *J*=8 Hz, 1H, Arom.), 8.53(dd, *J*=8, 8 Hz, 2H, Arom.), MS (m/z): 681(M⁺)

1b, mp: 104.5-105.2 °C, IR (KBr disk method): ν = 1688, 1651 (C=O), ¹H-NMR (300 MHz, CDCl₃): δ = 0.78-0.85(m, 12H, -CH₃), 1.16-1.58(m, 24H, Sn-(CH₂)₃-, -(CH₂)₂-), 1.69(m, 2H, -CH₂-), 4.12(t, *J*=8 Hz, 2H, N-CH₂), 7.57(t, *J*=8 Hz, 1H, Arom.), 7.72(d, *J*=8 Hz, 1H, Arom.), 7.77(d, *J*=8 Hz, 1H, Arom.), 8.27(d, *J*=8 Hz, 1H, Arom.), 8.32(dd, *J*=8, 8 Hz, 2H, Arom.), 8.37(d, *J*=8 Hz, 1H, Arom.), 8.50(dd, *J*=8, 8 Hz, 2H, Arom.), MS (m/z): 695(M⁺)

Naphthylperylene-dicarboximide derivatives (**3a,b**)

Naphthylperylene (**3a**) was prepared as follows. A solution of **1a** (0.50 g, 0.734 mmol), **2a** (0.25 g, 7.34 mmol), and Pd(PPh₃)₄ (0.042 g, 5 mol % of **1a**) in toluene (30 mL) was

refluxed for 4 d. The solvent was evaporated and the residue purified by column chromatography (silica gel, CH₂Cl₂ and THF) and recrystallization from ethanol to give **3a** as a red solid (0.38 g, 76.4 %). **3b** was prepared in 75.0 % yield from **1b** and **2b** similarly.

3a, IR (KBr disk method): ν =1687, 1649 (C=O), ¹H-NMR (300 MHz, CDCl₃): δ =0.86-0.89(m, 6H, -CH₃), 1.37-1.38(m, 8H, -(CH₂)₂-), 1.71(m, 4H, -CH₂-), 4.16(tt, J =8, 8 Hz, 4H, N-CH₂), 7.33(d, J =8 Hz, 1H, Arom.), 7.40(t, J =8 Hz, 1H, Arom.), 7.53(d, J =8 Hz, 1H, Arom.), 7.58(t, J =8 Hz, 1H, Arom.), 7.77(dd, J =8, 8 Hz, 2H, Arom.), 8.39-8.60(m, 7H, Arom.), 8.69(d, J =8 Hz, 1H, Arom.), MS (m/z): 656(M⁺)

3b, IR (KBr disk method): ν =1688, 1652 (C=O), ¹H-NMR (300 MHz, CDCl₃): δ =0.80-0.85(m, 6H, -CH₃), 1.28-1.40(m, 12H, -(CH₂)₂-), 1.70(m, 4H, -CH₂-), 4.16(tt, J =8, 8 Hz, 4H, N-CH₂), 7.32(d, J =8 Hz, 1H, Arom.), 7.41(t, J =8 Hz, 1H, Arom.), 7.53(d, J =8 Hz, 1H, Arom.), 7.57(t, J =8 Hz, 1H, Arom.), 7.78(dd, J =8, 8 Hz, 2H, Arom.), 8.36-8.59(m, 7H, Arom.), 8.69(d, J =8 Hz, 1H, Arom.), MS (m/z): 684(M⁺)

Terrylenebis(dicarboximide) derivatives (**4a,b**).

Terrylenebis(dicarboximide) (**4a**) was prepared as follows. Compound(**3a**)(0.50 g, 0.762 mmol), KOH (30 g, 0.53 mol), and ethanol (60 mL) were refluxed for 3 h. The dark blue melt was poured onto 2M-HCl, the precipitate removed by filtration, washed twice with boiling water and chloroform to give **4a** (0.46 g, 93.0 %). **4b** was prepared in 90.0 % yield from **3b** similarly.

N,N'-Terrylenebis(dicarboximide) derivative (**4a**), mp > 300 °C, IR (KBr disk method): ν =1688, 1652 (C=O), MS (m/z): 654(M⁺), HRMS calcd for C₄₄H₃₄N₂O₄ 654.2520, found 654.2526.

N,N'-Terrylenebis(dicarboximide) derivative (**4b**), mp > 300 °C, IR (KBr disk method): ν =1687, 1651 (C=O), MS (m/z): 682(M⁺), HRMS calcd for C₄₆H₃₄N₂O₄ 682.2832, found 682.2827.

REFERENCE

1. R. Nakazawa, N. Mutou, Y. Mizuta, A. Kawahara, E. Miyamoto, S. Tutumi, and T. Ikeda, K. Mizuhashi, *Nippon Kagaku Kaishi*, 1992, 1007.
2. M. Adachi and Y. Nagao, *Chem. Mater.*, 1999, **11**, 2107.
3. S. Tamura, Sony Inc., Japan Kokai 67450 (1999)(*Chem. Abstr.*, 1999, **130**, 244248f).
4. Y. Nagao, T. Naito, Y. Abe, and T. Misono, *Dyes and Pigments*, 1996, **32**, 71.
5. Y. Nagao and T. Misono, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1575.
6. Y. Nagao, Y. Abe and T. Misono, *Dyes and Pigments*, 1991, **16**, 19.
7. H. Quante and K. Mullen, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1323.
8. Y. Geerts, H. Quante, H. Plutz, R. Mahrt, M. Hopmeier, A. Bohm, and K. Mullen, *J. Mater. Chem.*, 1998, **8**, 2357.
9. F. O. Holtrup, G. R. J. Muller, H. Quante, S.D. Feyter, F.C.D. Schryver, and K. Mullen, *Chem. Eur. J.*, 1997, **3**, 219.
10. Y. Nagao, K. Tsuda, K. Kozawa, and T. Uchida, *Heterocycles*, 2001, **54**, 757.
11. J. Griffiths and K.J. Pender, *Dyes and Pigments*, 1982, **2**, 37.