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SYNTHESIS AND PROPERTIES OF AZA-PERYLENEDICARBOXIMIDE DERIVATIVE[≠]

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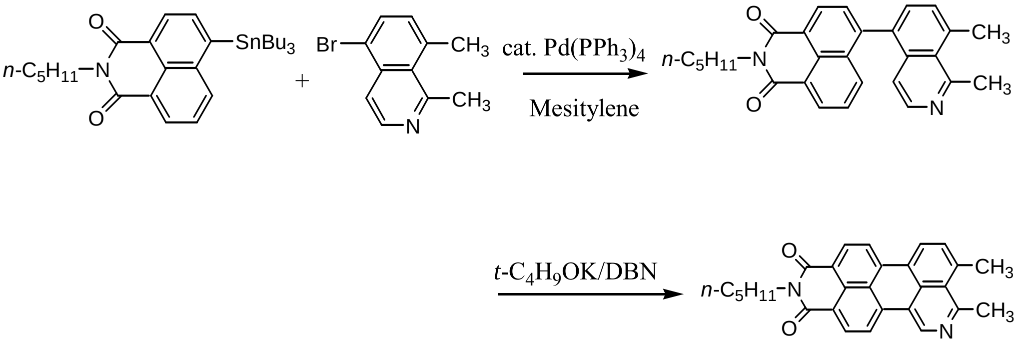
Abstract – Azaperylenedicarboximide derivative was prepared by coupling of *N*-pentyl-4-tributylstannylnaphthalene-1,8-dicarboximide with 4-bromo-1,8-dimethylisoquinoline in the presence of Pd(PPh_3)$_4$ and following ring closure reaction by using *t*-C_4H_9OK/DBN as base. Spectral properties of absorption and fluorescence in solution of the azaperylene derivative were investigated.

Perylene pigments (perylenedicarboximide derivatives) have high light fastness and heat stability. Recently some of them are used as not only pigments but also functional dyes for organic photoconductors in electrophotography, organic EL devices , and organic solar cell



Scheme 1

[≠] Dedicated to the memory of Professor Leo A. Paquette.

(photovoltaic cell).[1,2] In this study, paying attention to the usefulness of perylene pigments, the synthesis of azaperylene derivative (**4**) having N-atom in its perylene skelton was investigated.[3] (Scheme 1)

Preparation of 5-naphtyl-1,8-dimethylisoquinoline(3) and azaperylene-9,10-dicarboximide(4). *N*-Penthyl-4-tributylstannylnaphthalene-1,8-dicarboximide (**1**) was prepared from *N*-pentyl-4-bromo-1,8-naphthalenedicarboximide by using tributylstannyl replacement with hexabutylditin.[4,5] 5-Bromo-1,8-dimethylisoquinoline(**2**) was prepared from *o*-methylacetophenone by our previous method.[6] The naphthylisoquinoline derivative(**3)** was obtained in 35 % yield *via* heterocoupling reaction of **1** with **2** in the presence of $Pd(PPh_3)_4$. Then **3** was cyclized by using *t*-C_4H_9OK/DBN as base to give azaperylene derivative(**4**). **4** was obtained in good yield approximately 70 % by using base complex reagent (*t*-C_4H_9OK/DBN), which is used for the condensation of naphthalene derivatives to give perylene derivatives,[7] than the usual base(KOH). The absorption spectra of these compounds in $CHCl_3$ indicated the formation of azaperylene ring by showing λ max at 484 nm for **4** against 335 nm for **3**. The IR spectra of these compounds showed imide $\nu_{C=O}$ at 1657, 1697 and 1674, 1697. The molecular ion peak of these compounds (**3** and **4**) could be detected in MS spectra.

Properties of azaperylenedicarboximide derivative(4). The properties in absorption and fluorescence spectra and thermal stability of azaperylene derivative (**4**) were investigated. The absorption and emission maximum wavelength of **4** were listed in Table 1. The calculated maximum absorption λ_{max} of **4** was shown at 471 nm (oscillator strength f = 2.651) and λ_{max} of perylenemonoimide (analogous perylene derivative) was shown at 473 nm (f = 1.285). These calculated λ_{max} was obtained by PPP method when all alkyl substituent were displaced to H.[8,9] The observed λ_{max} of **4** was shown at 484 nm and the observed λ_{max} of perylenemonoimide was shown at 485 nm. There are almost no difference between the observed λ_{max} and the calculated λ_{max}.

As a general rule, the UV-Vis. absorption spectra of the aromatic heterocyclic compounds resemble those of the corresponding aromatic hydrocarbons very closely.[10,11] The same rule was found in perylene derivatives, and the absorption spectra of **4** is similar to that of analogous perylene derivative as indicated in Figure 1.

The absorption spectrum of **4** have a shoulder peak at 505 nm which imply the molecular association in solution because ^{1}H-NMR spectrum of 4 showed very complicated peaks.

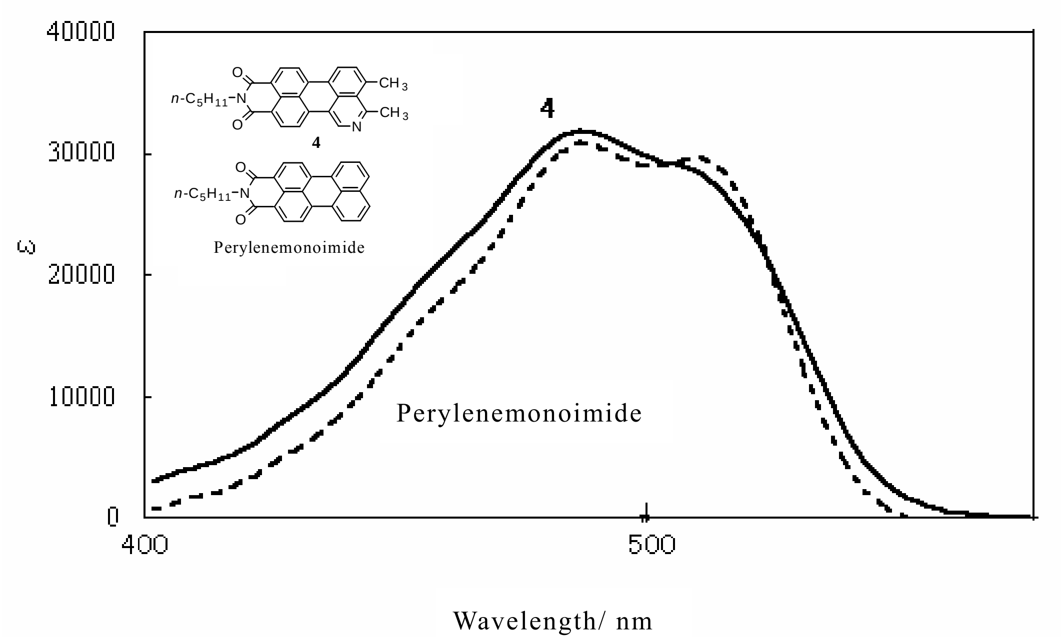
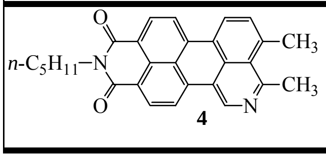


Figure 1 Visible absorption spectra of **4** and perylenemonoimide in $CHCl_3$

Table 1 Visible absorption and emission maximum wavelength of **4**

Compd	Absorption a)	Emission a)	
	λ max / nm	λ max /nm	Φ b)
 **4**	484 (ε : 3.2×10^4)	544	0.89

a) Solv.: $CHCl_3$

b) Fluoroscence quantum yield, reference perylene (Φ = 0.95)

The fluorescence spectrum of **4** in $CHCl_3$ was shown in Figure 2. The most strong excitation wavelength was at 491 nm and the maximum emission was shown at 544nm. The relative quantum yield was 0.89.

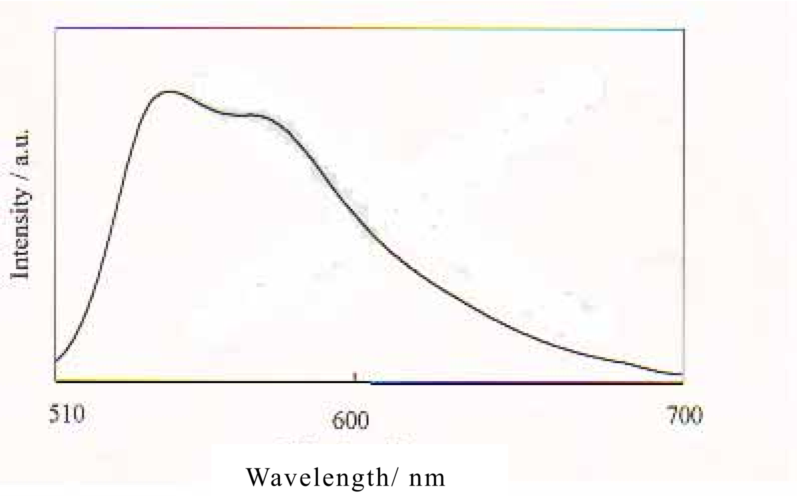


Figure 2 Emission spectrum of azaperylene derivative(**4**) in $CHCl_3$.
(Excitation wavelength: 491 nm)

The melting point of **4** was 239-240 ℃. The thermal decomposition point of **4** was 349 ℃ shown by the weight loss starting and its exothermic peak on the thermogravimetry (TG) and differential thermal analysis (DTA) curve. Then the azaperylene dye (**4**) has high stability to heat.

EXPERIMENTAL

MS: JEOL Mstation JMS-700 – UV/VIS: JASCO V-570 – Fluorescence spectra: JASCO FP-6200 – IR: JASCO FT/IR-410 – NMR: JEOL JMS-EX300 and JMS-EX500 – Melting points (uncorrected): MRK MP-MG – Thermal decomposition: Mac science WS002 (at a heating rate 10 $℃ min^{-1}$ in air)

4-Bromo-1,8-naphthaleneanhydride, pentylamine and *o*-methylacetophenon used were obtained commercially. *N*-Pentyl-4-bromonaphthalenedicarboximide[11] and 5-bromo-1,8-dimethylisoquinoline[6,13,14] were prepared according to the procedures reported.

_N_-Pentyl-4-tributhylstannylnaphthalene-1,8-dicarboximide (**1**)

A solution of _N_-pentyl-4-bromonaphthalene-1,8-dicarboximide (3.2 g, 9.2 mmol), hexabutylditin (9.0 g, 16 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.15 g, 0.13 mmol) in toluene(150 mL) was heated under reflux with stirring for 1 day. The toluene was removed in vacuo and the residue was chromatographed on silica gel by using benzene as eluent. After evaporation of the solvent, compound(**1**) (4.8 g, 92 %) was obtained as oil.

IR(KBr disk method): ν =1663, 1703 cm^{-1}(C=O), ^{1}H-NMR(300 MHz, $CDCl_3$): δ =0.86-0.94 (m, 12H, $-CH_3$), 1.25-1.41 (m, 16H, $-CH_2-CH_2-$), 1.52-1.60 (m ,6H, $-CH_2-$), 1.75 (m , 2H, $-CH_2-$), 4.18 (t, _J_=7.5 Hz, 2H , CH_2), 7.75 (t, _J_=8.5 Hz, 1H, arom.H), 8.05 (d, _J_=7.0 Hz, 1H, arom.H), 8.38 (d, _J_=8.5 Hz, 1H, arom.H), 8.49 (d, _J_=7.0 Hz, 1H, arom.H), 8.61 (d, _J_=8.5 Hz, 1H, arom.H), MS(m/z): $554(M-2)^+$, $556(M)^+$, $558(M+2)^+$

5-(_N_-Pentyl-1',8'-dicarboximide-5'-naphtyl)-1,8-dimethylisoquinoline(**3**)

A solution of tributhylstannylnaphthalene(**1**) (4.0 g, 7.2 mmol), 5-bromo-1,8-dimethyl-isoquinoline (2.2 g, 9.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.43 mmol) in mesitylene (150 mL) was heated under reflux with stirring for 3 day. The toluene was removed in vacuo and the residue was chromatographed on silica gel by using ethyl acetate as eluent. After evaporation of the solvent and subsequent recrystallization of the residue from methanol, compound(**3**) (1.1 g, 36 %) was obtained.

mp 175.5-176℃, IR(KBr disk method): ν =1657,1697 cm^{-1}(C=O), ^{1}H-NMR(300 MHz, $CDCl_3$): δ =0.86 (t, _J_=7.2 Hz, 3H, $-CH_3$), 1.36-1.37 (m, 4H, $-CH_2CH_2-$), 1.70(m, 2H, $-CH_2-$), 3.01 (s, 3H, $-CH_3$), 3.17 (s, 3H, $-CH_3$), 4.16 (t, _J_=7.6 Hz, 2H, $-CH_2$), 6.86 (d, _J_=6.0 Hz, 1H, arom.H), 7.44-7.52 (m, 3H, arom.H), 7.60(d, _J_=8.0 Hz, 1H, arom.H), 7.64(d, _J_=7.2 Hz, 1H, arom.H), 8.08 (d, _J_=6.0 Hz, 1H, arom.H), 8.55 (d, _J_=6.8 Hz, 1H, arom.H), 8.63 (d, _J_=7.2 Hz, 1H, arom.H), MS(m/z): $423(M)^+$, Anal. Calcd for $C_{28}H_{26}N_2O_2$: C 79.58, H 6.21, N 6.63, Found C 79.31, H 6.39, N 6.57

_N_-Pentyl-3,4-dimethylazaperylene-9,10-dicarboximide(**4**)

A mixture of potassium _t_-butoxide(2.0 g, 17.8×10^{-3} mol) and 1,5-diazabicyclo[4.3.0]non-5-ene (4.0 g, 32.3 mmol)was stirred at 140℃ for 1 h under N_2, and then, **3**(1.2 g, 2.8 mmol) was added and the mixture was stirred at the same temperature for an additional 6 h. The mixture was cooled to rt, water was added and filtered. The collected solid was washed with methanol and was chromatographed on silica gel by using ethyl acetate as eluent. After evaporation of the solvent compound (**4**) (0.8 g, 69 %) was obtained.

mp: 239-240 ℃, IR(KBr disk method): ν =1647,1697cm^{-1}(C=O), MS(m/z): 421(M^{+}), Anal. Calcd for $C_{28}H_{24}N_2O_2$: C 79.96, H 5.76, N 6.66, Found C 79.61, H 5.87, N 6.77

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