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SYNTHESIS AND SPECTRAL PROPERTIES OF AZA-TERRYLENE DICARBOXIMIDE DERIVATIVE

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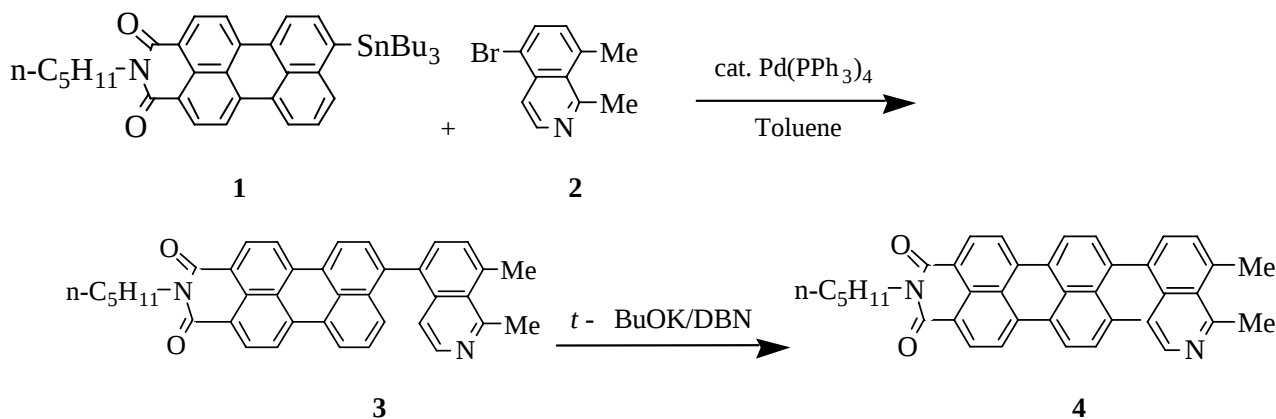
Abstract – Azaterrylene dicarboximide derivative was prepared by the coupling of *N*-pentyl-9-tributylstannylperylene-1,8-dicarboximide with 5-bromo-1,8-dimethylisoquinoline in the presence of Pd(PPh₃)₄ and following ring closure reaction by using *t*-BuOK/DBN. Spectral properties in solution were investigated and analyzed by molecular orbital method.

Perylene pigments have high fastness and stability to heat. Recently some of them are used as not only pigments but also functional dyes for organic solar cell, organic EL devices and organic photoconductors in electrophotography.^{1,2} As for terrylene which expands the skeleton further to the longer axis direction of a molecule, these derivatives have absorptions in the VIS and the near-IR region. These having near-IR region absorption in solid shows red emissions.³ These application as the organic solar cell and the pigment for organic EL are examined. It is reported in patent⁴ as the pigment for organic EL that stability, color purity and brightness are superior.

Furthermore, when the N atom is introduced into the skeleton of the molecule, it is known that light absorbance increases. Then, azaperylene or azaterrylene which introduces the N atom into the perylene or terrylene skeleton can be expected the increase of light absorbance. In addition, it is very interesting aromatic azahydrocarbons introducing the N atom into the skeleton indicate different properties compared with their parent's molecules. In our previous paper, the synthesis of azaperylene derivative and its spectral properties were reported.⁵ In this study, the synthesis of azaterrylene derivatives

≠ Dedicated to the memory of Professor Barry M. Trost

having one N-atom in terrylene's skeleton were investigated. (Scheme 1) Then its electronic spectrum was observed and the absorption maximum was assigned by the molecular orbital method.



Scheme 1

Preparation of *N*-pentyl-9-(1,8-dimethyl-5-isoquinoly)perylene-3,4-dicarboximide(3) and *N*-pentyl-3,4-dimethylazaterrylene-11,12-dicarboximide(4) SnBu₃ substituted compound (1) was prepared *via* five steps from 3,4,9,10- perylenetetracarboxylic dianhydride.^{3,6} The bromoisoquinoline (2) was prepared *via* three steps from *o*-methylacetophenone,^{7,8} Then, isoquinolyperylene (3) was prepared in 52.3 % yield by the heterocoupling reaction of 1 with 2 in the presence of Pd(PPh₃)₄. 3 was cyclized by using *t*-BuOK/DBN to obtain azaterrylene derivative (4). Synthesis could not succeed with the method by using KOH/EtOH solution which is used for the cyclization reaction in synthesizing terrylene derivative.³ But on the above-mentioned method by using *t*-BuOK/DBN 28.1% yield of 4 could be obtained. Similar cyclization using *t*-BuOK/DBN succeed in the synthesis of azaperylene or perylene derivatives.^{5,8} Yield and spectral data of 3 and 4 are listed in Table 1. The molecular ion peak of the compounds (3,4) could be detected in their MS spectra.

Table 1 Yield and Spectral Data of 3 and 4

Compd	Yield	VIS-nearIR		MS
	/%	λ /nm ^{c)}	λ /nm ^{d)}	/m/z(M ⁺) ^{e)}
3	52.3 ^{a)}	493, 515	626	546
4	28.1 ^{b)}	611	774	544

a) React. temp.: reflux(110 °C), React. time: 96 h, Molar ratio:1:2=1:1.1

b) React. temp.: 190 °C, React. time: 8 h

c) Solv.: CHCl₃ d) Solv.: conc.H₂SO₄ e) Ion mode:EI⁺

Azaterrylene derivative (4) is purple solid. In CHCl₃ solution it showed λ_{max} at 611 nm and in H₂SO₄ solution its λ_{max} shifted approximately 150 nm long wavelength to give absorption maximum at 774 nm.

Absorption spectra of azaterrylene dicarboximide derivative (4) Table 2 summarizes the maximum absorption $\lambda_{\max}$ of azaperylene derivatives and **4**. By comparison with the absorption of azaperylene derivative which has the same substituent, approximately 130 nm long wavelength $\lambda_{\max}$ was shown on the absorption spectrum of **4** in the CHCl_3 solvent. The $\lambda_{\max}$ has shifted due to the aromatic ring expanding to the longer axis direction of the azaperylene molecule (Figure 1).

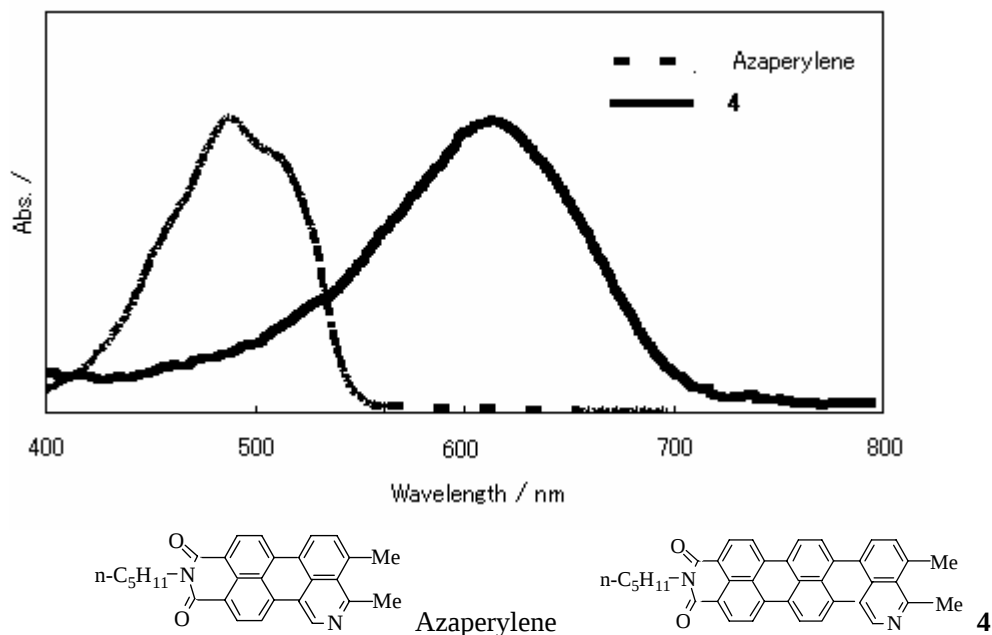
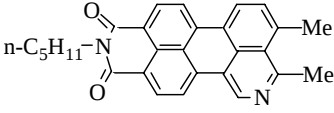
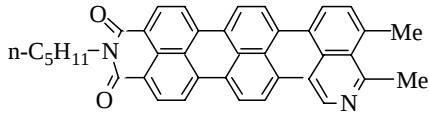


Figure 1 Electric Spectra of Azaperylene and **4** in CHCl_3

Table 2 Absorption Maximum of Azaperylene Derivative and **4**

Compd	VIS-nearIR
	$\lambda / \text{nm}^{\text{a)}$
 Azaperylene	484
 4	611

a) Solv.: CHCl_3

This long wavelength shift is resembling the case where the perylene derivative and the terrylene derivative are compared. In a preceding paper,¹⁰ we calculate the absorption spectra of perylene and terrylene dyes by MO calculation using the INDO/S method to analyze theoretically. Therefore we theoretically analyze the azaterrylene framework by the same method. Calculated absorption maxima of

terrylene diimide(TTCAI), azaterrylene diimide(10N-TTCAI), terrylene monoimide(TDCAI), and azaterrylene monoimide(4, 10N-TDCAI) are shown in Figure 2.

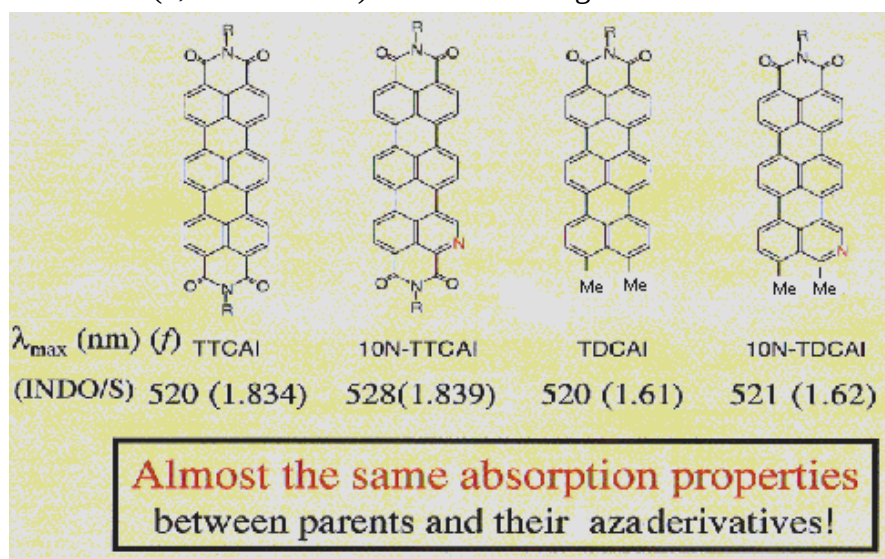


Figure 2 Calculated absorption maxima of azaterrylene and terrylene derivatives

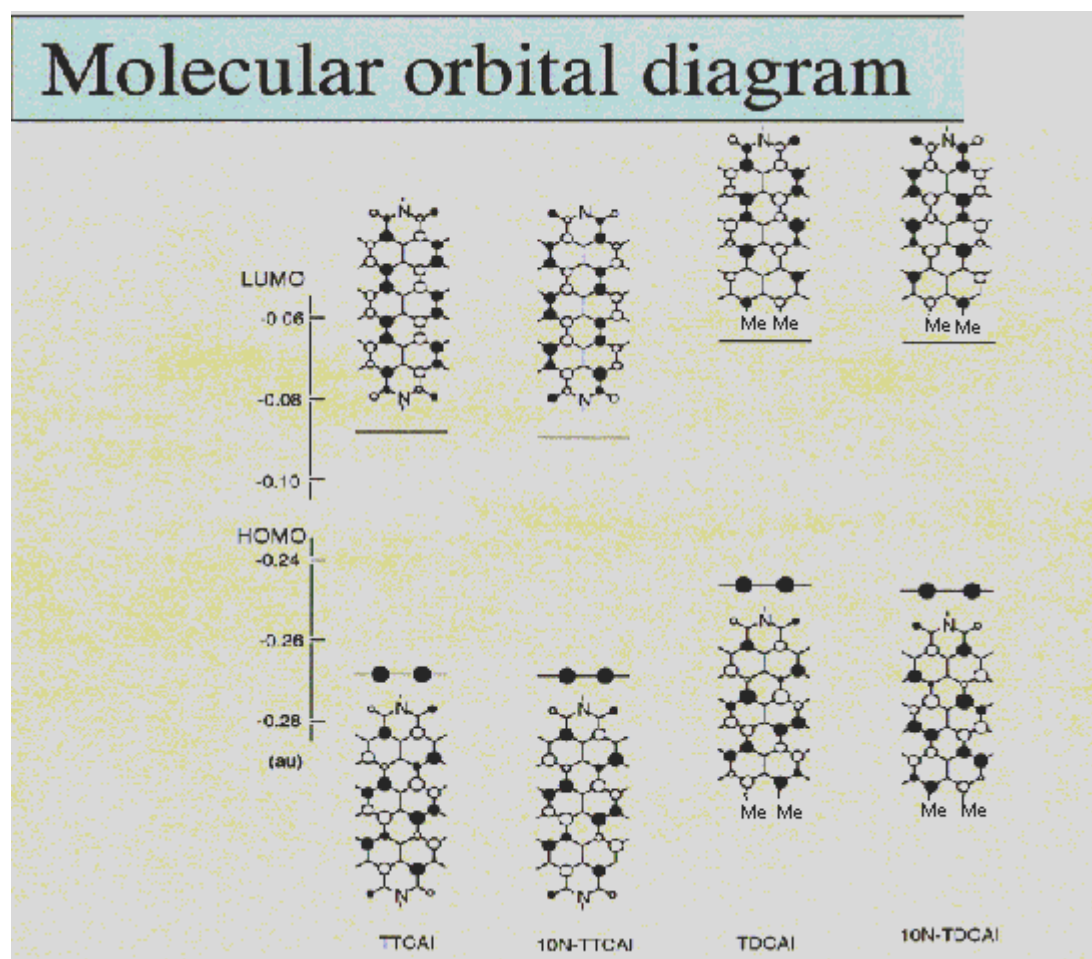


Figure 3 Molecular orbital diagram of azaterrylene and terrylene derivatives

Transition properties of these absorption maxima and other absorptions are shown in Table 3. These

absorption maxima are $\pi - \pi^*$ transitions and almost the same absorption properties between parents and aza-derivatives. Figure 3 illustrate HOMOs and LUMOs of these azaterrylene and terrylene derivatives with their energy levels. HOMO level and LUMO level between parents and their azaderivatives is scarcely affected. One more imide connections in TTCAI and 10N-TTCAI lower both HOMO and LUMO levels than TDCAI and 10N-TDCAI. Therefore, these absorption maxima are almost the same. The observed absorption maximum of TTCAI(650 nm)⁶ and 10N-TDCAI(**4**)(611 nm) are almost same, too. $n(\text{aza-N}) - \pi^*$ Transitions in 10N-TTCAI and 10N-TDCAI are shown at shorter wavelength(Table 3).

Table 3 Transition properties of azaterrylene derivatives

TTCAI $\lambda_{\max}(\text{nm})$	F^a	10N-TTCAI $\lambda_{\max}(\text{nm})$	F^a	TDCAI $\lambda_{\max}(\text{nm})$	F^a	10N-TDCAI $\lambda_{\max}(\text{nm})$	F^a	transition property
520	1.834	528	1.839	520	1.612	521	1.621	$\pi - \pi^*$ (main band) ^b
374	0.000	384	0.004	362	0.006	365	0.003	$\pi - \pi^*$ ^b
359	0.002	360	0.002	362	0.017	362	0.018	$\pi - \pi^*$ ^c
357	0.000	363	0.000	364	0.002	369	0.011	$\pi - \pi^*$
349	0.000	346	0.002	347	0.001	346	0.010	$\pi - \pi^*$ ^c
346	0.006	348	0.004	353	0.017	349	0.017	$\pi - \pi^*$ ^c
369	0.001	384	0.002	364	0.001	364	0.001	$n - \pi^*$
369	0.000	369	0.001					$n - \pi^*$
351	0.000	359	0.000	348	0.000	348	0.000	$n - \pi^*$
351	0.000	351	0.000					$n - \pi^*$
		250	0.003			261		$n(\text{aza-N}) - \pi^*$

a Oscillator strength.

b Correspond to the naphthalene $B_{2u}(^1L_a)$ transition.

c Correspond to the Naphthalene $B_{3u}(^1L_b)$ transition.

EXPERIMENTAL

MS: JEOL Mstation JMS-700 - UV/VIS: JASCO V-570 were used. 3,4,9,10-Perylenetetra-carboxylic dianhydride, pentylamine and *o*-methylacetophenone were obtained commercially. *N*-Pentyl-9-tributylstannylperylene-1,8-dicarboximide^{3,6} and 5-bromo-1,8-dimethylisoquinoline were prepared according to the procedures reported.^{7,8} The absorption spectra were calculated by the INDO/S method in our preceding paper.⁹

N-Pentyl-9-(1,8-dimethyl-5-isoquinolyl)perylene-3,4-dicarboximide (**3**)

N-Pentyl-9-tributylstannylperylene-1,8-dicarboximide (**1**) (0.62 g, 9.11×10^{-4} mol), 5-bromo-1,8-dimethylisoquinoline (0.25 g, 1.06×10^{-3} mol) and tetrakis(triphenylphosphine)palladium(0) (90 mg, 8.6

mol%) in toluene (30 mL) heated under reflux with stirring for 4 days. Toluene was removed in vacuo and the residue was chromatographed on silica gel by using dichloroethane as eluent. After evaporation of the solvent and subsequent recrystallization of the residue from ethanol, compound (**3**)(0.26 g, 52.8 %) was obtained, dark red powder, mp > 300 °C.

IR(KBr disk method): ν = 1695, 1653 cm^{-1} (C=O), 1596, 1572, 1558, 1541, 1506, 1458 cm^{-1} (C=N, C=C), ^1H -NMR (300 MHz, CDCl_3): δ = 0.86 (m, 3H, Alkyl- CH_3), 1.34 ~ 1.35 (m, 4H, $-(\text{CH}_2)_2-$), 1.68 (m, 2H, $-\text{CH}_2-$), 3.01 (s, 3H, Naphthyl- CH_3), 3.18 (s, 3H, Naphthyl- CH_3), 4.09 (t, J =7.5 Hz, 2H, N- CH_2-), 7.04 (d, J =5.7 Hz, 1H, Arom-H), 7.29 (d, J =7.2 Hz, 1H, Arom-H), 7.35 (d, J =7.2 Hz, 1H, Arom-H), 7.49 ~ 7.54 (m, 3H, Arom-H), 8.10 (d, J =5.7 Hz, 1H, Arom-H), 8.26 ~ 8.34 (m, 3H, Arom-H), 8.41 ~ 8.49 (m, 3H, Arom-H), MS(m/z): 546(M)⁺, HRMS Calcd for $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_2$ 546.2308, found M^+ 546.2311.

***N*-Pentyl-3,4-dimethylazaterrylene-11,12-dicarboximide(**4**)**

Potassium *t*-butoxide (8.1 g, 7.2×10^{-2} mol) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)(9.1 g, 7.3×10^{-2} mol) stirred at 190 °C for 1 h under N_2 , and then, **3** (0.5 g, 1.15×10^{-4} mol) was added and stirred at the same temperature for an additional 8 hours. The mixture was cooled to rt, water was added and filtrated. The collected solid was washed with methanol and was chromatographed on silica gel by using dichloromethane and THF as eluent. After evaporation of the solvent compound (**4**) (0.14 g, 28.1%) was obtained, dark purple powder, mp > 300 °C.

IR(KBr disk method): ν = 1697, 1654 cm^{-1} (C=O), MS(m/z): 544(M)⁺, HRMS Calcd for $\text{C}_{38}\text{H}_{28}\text{N}_2\text{O}_2$ 544.2152, found M^+ 544.2145.

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