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Synthesis of pentacene-, tetracene- and anthracene bisimides using double-cyclization reaction mediated by bismuth(III) triflate†

Shuhei Katsuta,^a Kazuki Tanaka,^a Yukihiro Maruya,^b Shigeki Mori,^c Sadahiro Masuo,^{de} Tetsuo Okujima,^f Hidemitsu Uno,^f Ken-ichi Nakayama^{be} and Hiroko Yamada^{*ae}

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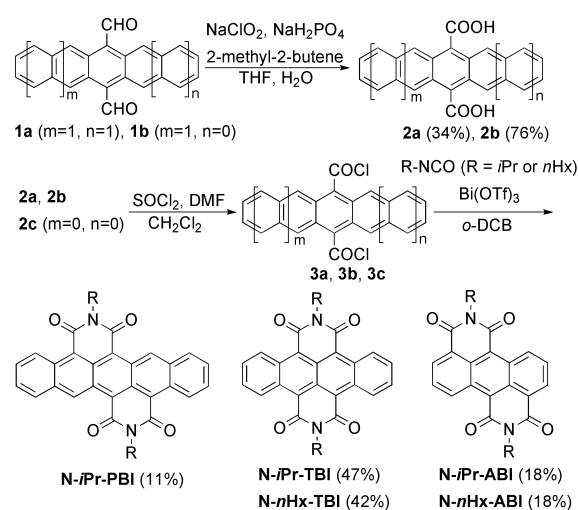
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Novel bisimide-fused acenes were synthesized via bismuth triflate mediated double-cyclization reaction of acid chlorides and isocyanates. Their optical and electrical properties revealed significantly smaller HOMO-LUMO gaps compared with those of their parent acenes. Fabricated OFET based on tetracene bisimide showed *n*-type OFET outputs.

Synthesis of π -expanded dyes having lower HOMO-LUMO gaps with higher stability is an important topic of current material science due to their potential applications in the field of organic electronic devices such as organic field-effect transistors (OFET) or organic photovoltaic cells (OPV).¹ Among these dyes, rylene bisimides represented by perylene bisimides can be considered as poly(perinaphthalene)bisimides and have been well researched due to their high optical properties, stability and accessibility.² In sharp contrast, only a few types of acenes having imide groups at *peri*-position have been reported due to the synthetic difficulties.³ Introduction of electron withdrawing groups to *peri*-positions are known to change the electronic and optical properties of acenes drastically. Thus specific properties would be expected for the acene bisimides. Very recently, Wudl *et al.* reported the synthesis of anthracene-1,9:5,10-bisimides (described as **ABI** in this communication)⁴ and Wu *et al.* have synthesized tetracene-4,5- or -5,6-monoimide from 1,2,3,4-tetrahydrotetracene.⁵ However the synthesis of pentacene or naphthacene with two imide substituents at *peri*-positions of central phenyl rings have yet to be achieved and only pentacene-2,3:9,10-bisimides, were reported by Chi *et al.*⁶ and Takahashi *et al.*⁷ independently.

In our previous research, a simple and efficient synthesis of

6,13-diformylpentacene and 5,12-diformyltetracene by using oxidative C-C bond cleavage-reaction of corresponding precursors has been reported.⁸ 6,13-Diformylpentacene and 5,12-diformyltetracene are useful synthetic intermediates for further functionalization such as oxidation, reduction or cyclization reactions. Here we will report an oxidation of 6, 13-diformylpentacene and 5,12-diformyltetracene to the corresponding dicarboxylic acids and their subsequent cyclization with isocyanates⁹ to give pentacene-5,6:12,13-bisimide (**PBI**) and tetracene-5,6:11,12-bisimide (**TBI**) successfully. We also applied the same strategy for the synthesis of anthracene-1,9:5,10-bisimide (**ABI**) from anthracene-9,10-dicarboxylic acid.



Scheme 1 Synthesis of pentacene-, tetracene- and anthracene bisimides.

Synthesis of **PBI**, **TBI** and **ABI** is shown in Scheme 1. Pinnick oxidation of **1a** and **1b** afforded dicarboxylic acids **2a** and **2b**. Anthracene dicarboxylic acid **2c** was prepared following a literature method.¹⁰ Dicarboxylic acids **2a-c** were then converted to corresponding acid chlorides **3a-c** quantitatively and they were used to the following reaction without purification. Reaction conditions of acid chloride **3b** and isopropyl isocyanate with protic or Lewis acids were investigated (Table S1). As a result of the screening, bismuth triflate¹¹ was suitable as an efficient Lewis acid for the cyclization reaction to give N,N'-di-*i*-propyl-TBI (**N-iPr-TBI**) in 47% yield. In the same reaction condition **N-iPr-PBI** and **N-iPr-ABI** were obtained in 11% and 18% yields as single

^a Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, 630-0192, Japan. E-mail: hyamada@ms.naist.jp; Fax: +081-743-72-6042; Tel: +081-743-72-6041

^b Department of Electrical Devices, Graduate School of Science and Engineering, Yamagata University, Yonezawa, 992-8510, Japan

^c Department of Molecular Science, Integrated Center for Sciences, Ehime University, Matsuyama 790-8577, Japan

^d Department of Chemistry, School of Science and Technology, Kwansai Gakuin University, Sanda, 669-1337, Japan

^e CREST, JST, Chiyoda-ku, 102-0075, Japan

^f Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama, 790-8577, Japan

† Electronic Supplementary Information (ESI) available. Experimental details for the synthesis, OFET measurements and Figure S1-3. See DOI: 10.1039/b000000x/

isomers. We have also succeeded in the synthesis of N,N'-di-*n*-hexyl-TBI (**N-*n*Hx-TBI**) and **N-*n*Hx-ABI** in 42% and 18% yields, respectively.

Single crystals of **N-*i*Pr-TBI** and **N-*n*Hx-TBI** were obtained as dark blue needles by a slow evaporation of chloroform from the mother liquor. Single-crystal X-ray diffraction studies of **N-*n*Hx-TBI** indicated two crystallographically independent molecules existed in a unit cell (Fig. 1a and Figure S1).[‡] Tetracene planes were sigmoidal and 6-membered imide rings were tilted from the planes of the central naphthalenes. The angles between the plane of central naphthalene the plane made by two carbonyl carbon and nitrogen atoms was 16.65° for molecule 1 and 13.14° for molecule 2. The two species alternately packed to make a face-to-face slipped 1-dimensional π -stacking structure with a minimum interplanar spacing of 3.260(8) Å (Fig. 1b). This structure with relatively short intermolecular distance is caused by strong alkyl chain interaction between neighboring molecules and the hydrogen bonding between peripheral phenyl proton and the neighboring oxygen atom of the imide group. For **N-*i*Pr-TBI** acene planes and hexagonal imide planes are twisted (Fig. 1c and Figure S2). They are packed to make a face-to-face slipped 1-dimensional π -stacking structure, and a minimum interplanar spacing between tetracene moieties was 3.358(4) Å.¹² The neighboring lines are placed in a zigzag shape to make ridges with *i*Pr groups and there is no CH- π interaction between tetracene planes.

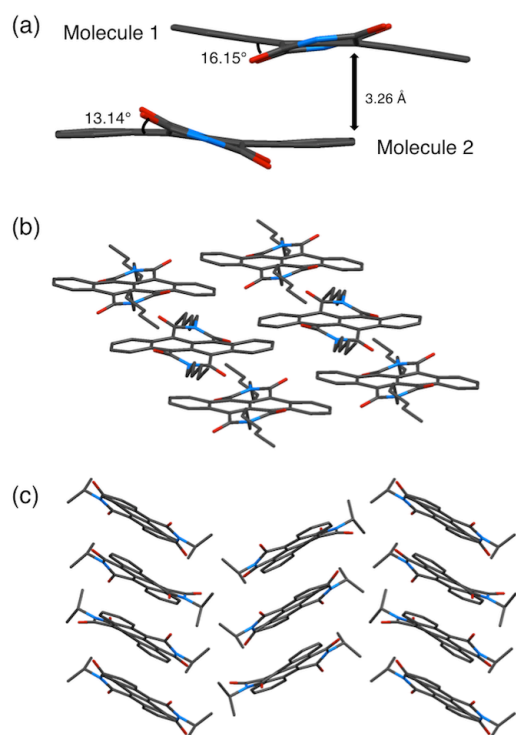


Fig. 1 (a) X-Ray crystallographic structures of **N-*n*Hx-TBI**. *n*-Hexyl groups are omitted for clarity; (b) packing structure of **N-*n*Hx-TBI**; (c) packing structure of **N-*i*Pr-TBI**. Hydrogen atoms are omitted for clarity.

The absorption and fluorescence spectra of acene bisimides in chloroform are shown in Figure 2 and Table 1. The absorbance maxima of **N-*i*Pr-ABI**, **N-*i*Pr-TBI** and **N-*i*Pr-PBI** are significantly red-shifted by 101, 150, and 167 nm relative to

parent anthracene, tetracene, and pentacene, respectively. This is due to the efficient π -conjugation and donor-acceptor interaction of the imide groups with the acene cores. To the best of our knowledge, this is the first example of the pentacene with no aryl- or ethynyl-substituents having the absorption edge over 800 nm. The broad absorption bands of **N-*i*Pr-PBI** and **N-*i*Pr-TBI** in visible light region indicate the potential application of these dyes as active layers in organic photovoltaic cells. The HOMO-LUMO gaps (E_g) calculated from the edge of the absorption are as follows, **N-*i*Pr-ABI**: 2.45 eV; **N-*i*Pr-TBI**: 1.83 eV; **N-*i*Pr-PBI**: 1.48 eV. The absolute fluorescence quantum yields (QYs) of **N-*i*Pr-ABI** and **N-*i*Pr-TBI** in chloroform are 0.78 and 0.28, respectively. The time profile of their singlet excited states in CHCl_3 excited at 465 nm with 100 ps pulse are shown in Figure S3. The fluorescence lifetimes (τ s) of **N-*i*Pr-ABI** and **N-*i*Pr-TBI** were 8.2 and 10.3 ns, respectively (Table 1). **N-*i*Pr-ABI** showed solid-state emission with QY of 0.18. Strong fluorescence of **N-*i*Pr-ABI** is attractive property for use as an emissive material in organic light emissive diodes. Fluorescence of **N-*i*Pr-PBI** was not detected under air or nitrogen.

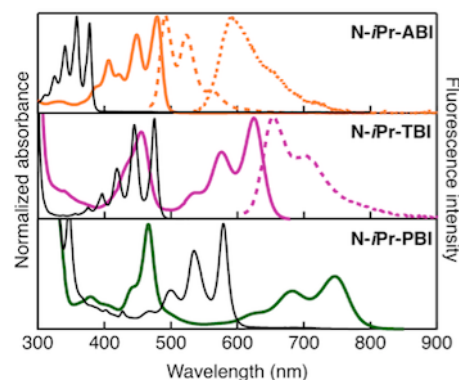


Fig. 2 UV-vis absorption and fluorescence spectra of **N-*i*Pr-ABI**, **N-*i*Pr-TBI**, **N-*i*Pr-PBI**, and parent acenes. Coloured lines: absorption of acene bisimides in chloroform; black lines: absorption of parent acenes, anthracene and tetracene in chloroform and pentacene in chlorobenzene; dashed lines: fluorescence in chloroform; dotted lines: fluorescence in solid state.

Table 1 Summary of optical properties of acene bisimides in CHCl_3 .

Compd	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}$	QY ($\lambda_{\text{ex}}/\text{nm}$)	τ / ns
N-<i>i</i>Pr-ABI	479 (19452), 449 (15741), 406 (10557)	491, 524, 560, 590 ^a	0.78 (449), 0.18 (449) ^a	8.2
	N-<i>i</i>Pr-TBI	624 (13929), 576 (9249), 455 (12027)	653, 703	0.28 (576)
N-<i>i</i>Pr-PBI	746 (9874), 682 (7124), 466 (19687)	-	-	-

^a Values in solid state.

The electrochemical properties of the acene bisimides were investigated by cyclic voltammetry, as shown in Figure S4 and summarized in Table 2. In all compounds, two reversible reduction peaks were observed, and the first reduction potentials are as follows; **N-*i*Pr-ABI** (-1.02 V vs Fc/Fc^+) **N-*i*Pr-TBI** (-0.74 V) and **N-*i*Pr-PBI** (-0.68 V) The LUMO levels of acene bisimides are determined by their onset reduction potentials. Oxidation potentials were not observed under this experimental condition, so HOMO levels were estimated from the LUMO level

and E_g values. HOMO levels of **N-*i*Pr-ABI**, **N-*i*Pr-TBI** and **N-*i*Pr-PBI** were deeper than anthracene, tetracene and pentacene by 0.76, 0.79 and 0.77 eV, respectively. Thus, their stabilities toward oxygen are expected to be improved due to its low HOMO levels. **N-*i*Pr-TBI** and **N-*i*Pr-PBI** show similar HOMO and LUMO levels of 5,12-dicyanotetracene (HOMO: 5.97 eV; LUMO: 4.00 eV) and 6,13-dicyanopentacene (HOMO: 5.77 eV; LUMO: 4.14 eV). These cyanated acenes showed ambipolar FET properties, thus **TBI** and **PBI** may show ambipolar properties. **N-*i*Pr-ABI** has similar LUMO level with perylene bisimide (LUMO: 3.8 eV)^{1d}, which is a typical *n*-type semiconductor. Thus **ABI** is expected to work as an *n*-type semiconductor.

Table 2 Summary of electrochemical properties of acene bisimides

Compd	E_{RED} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c	E_g (eV) ^d
N-<i>i</i>Pr-ABI	-1.02, -1.39	6.31	3.86	2.45
N-<i>i</i>Pr-TBI	-0.74, -1.08	5.96	4.13	1.83
N-<i>i</i>Pr-PBI	-0.68, -1.00	5.65	4.17	1.48

^aV vs Fc/Fc⁺. Obtained by cyclic voltammetry. See Fig. 3. ^bEstimated from LUMO levels and E_g . ^cCalculated by measuring the difference between the onset of reduction and the half-wave potential of the ferrocene standard (4.8 eV). ^dObtained from the edge of the absorption spectra.

Top-contact field-effect transistor was fabricated by vapor deposition (0.2 Å s⁻¹) of **N-*n*Hx-TBI** with a thickness of 60 nm onto HMDS treated SiO₂/Si substrate. Au was used as electrode. The output of device in nitrogen atmosphere is shown in Figure 3 and S5 (A detail of experimental condition is described in ESI†). Contrary to our initial expectation, **N-*n*Hx-TBI** showed typical *n*-type response. Thus 3.3×10⁻³ cm² V⁻¹ s⁻¹ of electron mobility, 5.3×10³ of on/off ratio and 11.6 V of threshold voltage was observed. XRD pattern of **N-*n*Hx-TBI** on the surfaces treated with HMDS are shown in Figure S6. A peak was observed at 2θ = 6.826°, which corresponded to an interplanar distance of 12.94 Å for **N-*n*Hx-TBI**. This value is close to the molecular length along the tetracene core of **N-*n*Hx-TBI** (11.4 Å). The **N-*n*Hx-TBI** is expected to stand perpendicular to the surface. AFM image of the thin film is shown in Figure S7. **N-*n*Hx-TBI** formed the flat thin film with 5 nm of roughness.

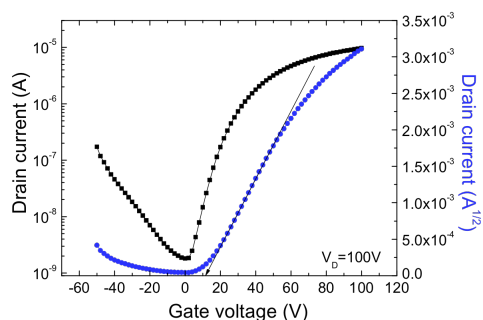


Fig. 3 OFET output of **N-*n*Hx-TBI** on HMDS-treated substrate.

Conclusions

Synthesis of pentacene-, tetracene-, and anthracene-bisimide have been successfully achieved by bismuth triflate-mediated double-cyclization reaction. These acene bisimides showed significantly low HOMO and LUMO levels relative to parent acenes. The HOMO-LUMO gap of **N-*i*Pr-PBI** was 1.48 eV and the edge of

the absorption band reached over 800 nm. **N-*n*Hx-TBI** showed *n*-type OFET performance with 10⁻³ cm² V⁻¹ s⁻¹ of electron mobility. Further derivatization of the acene bisimides is under investigation for the developments of new *n*-type semiconducting materials.

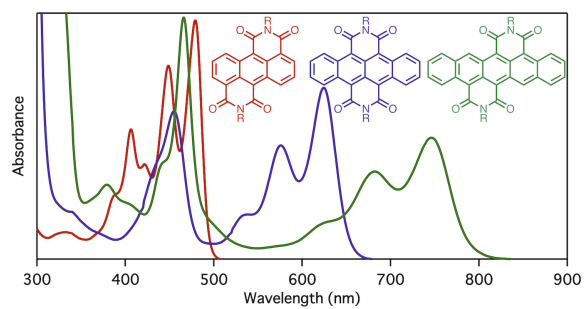
Acknowledgement

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Notes and references

- ‡ Crystal data for **N-*n*Hx-TBI** (C₃₄H₃₄N₂O₄): $M_w=534.65$, triclinic $P\bar{1}$, $a=10.0736(10)$, $b=11.1410(12)$, $c=13.7743(11)$ Å, $\alpha=76.275(5)^\circ$, $\beta=175.947(5)^\circ$, $\gamma=64.225(6)^\circ$, $V=1335.0(3)$ Å³, $T=100(2)$ K, $Z=2$. 15037 reflections were measured, and $R_{merge}=0.0989$, $R_1=0.0839$ (2164, $I>2\sigma(I)$), $wR_2(\text{all})=0.2334$ (4605), $GOF=1.025$. Crystal data for **N-*i*Pr-TBI** (C₂₈H₂₂N₂O₄): $M_w=450.49$, monoclinic $P2_1/c$, $a=11.399(4)$, $b=21.609(8)$, $c=13.165(6)$ Å, $\beta=104.728(9)^\circ$, $V=3136(2)$ Å³, $T=100(2)$ K, $Z=6$. 51398 reflections were measured, and $R_{merge}=0.0835$, $R_1=0.0982$ (6162, $I>2\sigma(I)$), $wR_2(\text{all})=0.0982$ (7180), $GOF=1.107$. CCDC-822760 (**N-*n*Hx-TBI**) and CCDC-822759 (**N-*i*Pr-TBI**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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TOC



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New pentacene and naphthacene bisimides were first synthesized and the naphthacene bisimide showed n-type OFET performance.