

Synthesis, Properties, and Ambipolar Organic Field-Effect Transistor Performances of Symmetrically Cyanated Pentacene and Naphthacene as Air-Stable Acene Derivatives

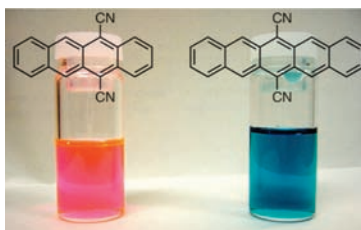
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ABSTRACT



5,12-Dicyanonaphthacene and 6,13-dicyanopentacene have been synthesized for the first time. The LUMO and HOMO levels are deepened as predicted and fabricated organic field-effect transistors (OFETs) showed ambipolar responses with carrier mobilities of $10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$.

Pentacene- and naphthacene-based organic field-effect transistors (OFETs) have attracted much attention as thin and flexible paper-like alternatives for silicon-based transistors.¹ Various acene-based transistors have been fabricated in the past few years that show good hole carrier mobilities.² However, to date, only a few pentacene compounds have been reported as n-type semiconducting acene molecules.³ For the development of good n-type semiconducting materials, a deep LUMO level is necessary

and introduction of electron-withdrawing groups such as cyano and fluorine groups to the acene structure is thought

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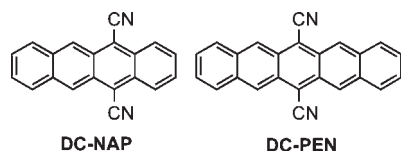
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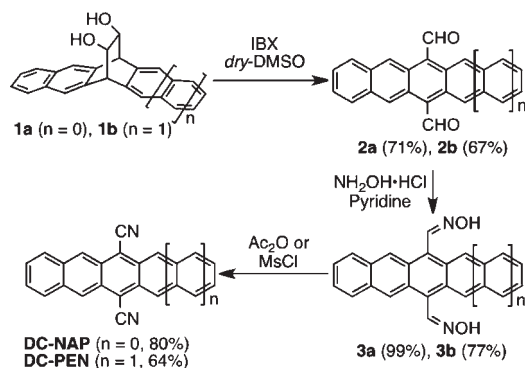
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to be effective in this regard. Chao,⁴ Miller,⁵ and Kuo⁶ have predicted that cyanated pentacenes should be quite amenable for use as n-type organic semiconductors because of their deep LUMO and narrower HOMO–LUMO gap (E_g). However the derivatization of pentacene is quite difficult due to its insolubility in common organic solvents and only a few types of cyanated acenes have been prepared.⁷ Even the simplest 6,13-dicyanopentacene and 5,12-dicyanonaphthacene have not been achieved due to their synthetic difficulties.



In this paper, we present the novel synthesis, properties, and OFET performances of 5,12-dicyanonaphthacene (**DC-NAP**) and 6,13-dicyanopentacene (**DC-PEN**). In the **DC-NAP** and **DC-PEN** structures, the most reactive *peri*-positions are effectively cyanated. To the best of our knowledge this is the first report on the synthesis of symmetrically cyanated pentacene.

Scheme 1. Synthesis of **DC-NAP** and **DC-PEN**



The synthesis of **DC-NAP** and **DC-PEN** is shown in Scheme 1. Diols **1a** and **1b** were easily prepared in gram scale quantities following literature procedures.⁸ Previously, Murdock et al. reported the conversion of **1a** to **2a** using $\text{Pb}(\text{OAc})_4$ with AcOH in 20% yield.⁹ However, this reaction was not applicable to the conversion of **1b** to **2b**. Thus, we used *o*-iodoxybenzoic acid (IBX) mediated oxidative cleavage reactions of **1a** and **1b**, which afforded 5,12-diformylnaphthacene **2a** and 6,13-diformylpentacene

2b in 71% and 67% yields, respectively. In general, IBX does not cleave vicinal 1,2-diols,¹⁰ although strained and sterically restricted *syn* 1,2-diols **1a** and **1b** were oxidized to give dialdehydes **2a** and **2b** via C–C bond cleavages.¹¹ **2a** and **2b** are useful intermediates for various chemical modifications such as oxidations, reductions, and condensations. The reaction of **2a** with $\text{NH}_2\text{OH} \cdot \text{HCl}$ in pyridine gave 5,12-dihydroxyiminomethylnaphthacene **3a** in 99% yield, which was then treated with Ac_2O or MsCl to afford **DC-NAP** in 80% yield. In a similar manner, **DC-PEN** was obtained in 33% overall yield from **1b**.

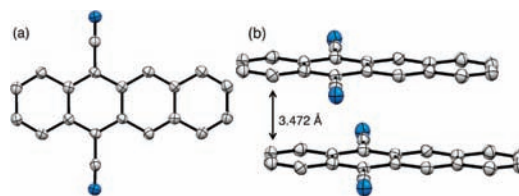


Figure 1. (a) ORTEP drawing of **DC-NAP** and (b) crystal structure of **DC-NAP**. $a = 3.79021(12)$ Å, $b = 12.8608(4)$ Å, $c = 13.5027(4)$ Å, $\alpha = 94.054(2)^\circ$, $\beta = 92.358(2)^\circ$, $\gamma = 91.872(2)^\circ$, $Z = 2$.

Single crystals of **DC-NAP** (Figure 1) were obtained as red needles from slow diffusion of chlorobenzene into a solution of **DC-NAP** in chloroform. The structure of **DC-NAP** is planar as was observed for naphthacene. The CN group is slightly bent in plane relative to the peripheral phenyl group, but not to the naphthyl group: angles of CN groups to the phenyl ring are $119.4(2)^\circ$ and $117.5(2)^\circ$ and the angles of C–C–N are $178.5(3)^\circ$ and $178.2(3)^\circ$, respectively. In sharp contrast to naphthacene, which forms a herringbone structure,¹² the crystal structure of **DC-NAP** is a face-to-face slipped π -stacking structure with an intermolecular distance of 3.472 Å. 5-Cyanonaphthacene is known to adopt a herringbone structure but 5,11-dicyanonaphthacene has been reported to adopt the face-to-face slipped π -stacking structure, which is similar to our result.^{7a}

The absorption and fluorescence spectra of dicyano acenes in chloroform are shown in Figure 2 and in Table S1 in the Supporting Information. The absorbance maxima of **DC-NAP** and **DC-PEN** are significantly red-shifted by 65 and 74 nm relative to parent naphthacene and pentacene.¹³ This is due to the efficient π -conjugation of

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(13) Because of the low solubility in chloroform, the absorption spectrum of pentacene was measured in chlorobenzene.

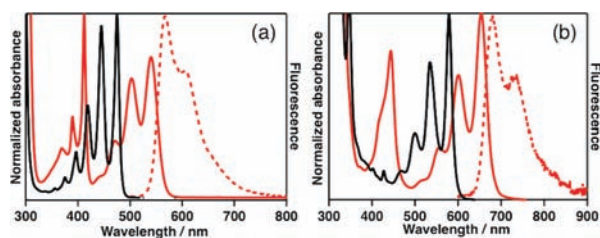


Figure 2. Normalized absorption spectra (red line) and fluorescence spectra (red dotted line) of (a) **DC-NAP** and (b) **DC-PEN** in chloroform. Black lines indicate the normalized absorption spectra of (a) naphthalene in chloroform and (b) pentacene in chlorobenzene.

the two cyano groups with the acene cores. The absolute fluorescence quantum yields of **DC-NAP** and **DC-PEN** in chloroform are 0.44 and 0.12, respectively.

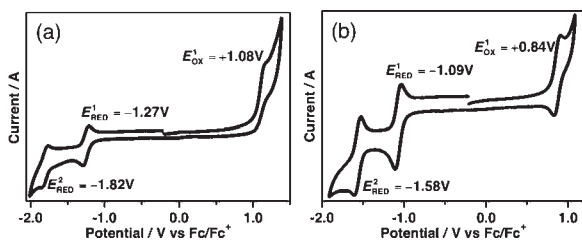


Figure 3. Cyclic voltammograms of (a) **DC-NAP** and (b) **DC-PEN** in dichloromethane (1 mM) (0.1 M Bu_4NPF_6 as supporting electrolyte; Ag/AgNO_3 as reference electrode; glassy carbon as working electrode; Pt wire as counter electrode; scan rate of 0.1 V/s).

The electrochemical properties of the dicyano acenes were investigated by cyclic voltammetry, as shown in Figure 3 and Table 1. Two reversible reduction peaks are observed in both **DC-NAP** and **DC-PEN**, and the reduction potentials of **DC-NAP** (-1.27 V vs Fc/Fc^+) and **DC-PEN** (-1.09 V vs Fc/Fc^+) have values similar to those of perfluoronaphthalene^{3c} (-1.49 V vs Fc/Fc^+) and

Table 1. Electrochemical Properties of **DC-NAP**, **DC-PEN**, Naphthalene, and Pentacene

compd	E_{OX} (V) ^a	E_{RED} (V) ^a	HOMO (eV) ^b	LUMO (eV) ^c	E_g (eV) ^d
DC-NAP	+1.08	-1.27	5.97	4.00	1.97
		-1.82			
DC-PEN	+0.84	-1.09	5.77	4.14	1.63
		-1.58			
naphthalene			5.14	2.40	2.74
pentacene			4.88	2.70	2.18

^a The values were obtained by cyclic voltammetry, V vs Fc/Fc^+ . See Figure 3 for experimental details. ^b The values were obtained by ionization potentials of the film. ^c The values were obtained from HOMO levels and E_g . ^d The values were obtained from the edge of the absorption spectra of the deposited film.

perfluoropentacene^{3d} (-1.13 V vs Fc/Fc^+), which are known as n-type semiconductor materials. The HOMO levels of dicyano acenes in thin films are also determined by their ionization potentials with those of naphthalene and pentacene, as shown in Table 1 and in Figure S1 in the Supporting Information. HOMO–LUMO gap energies (E_g) are estimated from wavelengths of the edge of the absorption spectra (Figure S2, Supporting Information) and LUMO levels were calculated from the HOMO level and E_g . HOMO levels of **DC-NAP** and **DC-PEN** are deeper than those of naphthalene and pentacene by 0.83 and 0.89 eV, respectively. Thus, their stabilities toward oxygen are expected to be improved. The LUMO levels of **DC-NAP** and **DC-PEN** are 4.00 and 4.14 eV, respectively, and are similar to those of C_{60} , a well-known n-type semiconductor. On the basis of their stable anionic states and low LUMO levels, **DC-NAP** and **DC-PEN** are expected to function as n-type semiconductors.

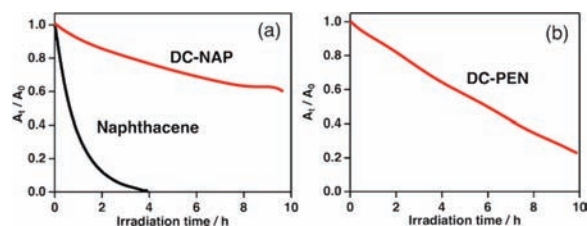


Figure 4. Stability of (a) **DC-NAP** and (b) **DC-PEN** toward oxidation in chloroform (A_0 : absorption intensity before photoirradiation; A_t : absorption intensity during photoirradiation). Initial concentrations of acenes are as follows: **DC-NAP**, 6.6×10^{-2} mM; **DC-PEN**, 7.0×10^{-2} mM; and naphthalene, 6.5×10^{-2} mM. The absorbance intensities were measured every 30 s.

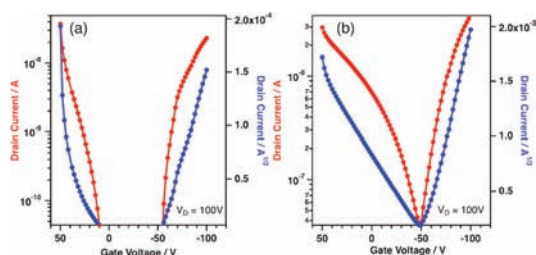
The stability of the dicyano acenes toward oxidative degradation was investigated next (Figure 4). The solution of **DC-NAP** (6.6×10^{-2} mM) or **DC-PEN** (7.0×10^{-2} mM) in chloroform was irradiated in a quartz cell (light pass: 1 cm) with a white light bulb (light intensity: 60 W; light-distance: 25 cm) under air. The decrease in the intensity of the absorption maximum was measured at intervals of 30 s during photoirradiation. In comparison to the parent acenes, the degradation rates of the dicyano acenes were significantly slower. **DC-NAP** and **DC-PEN** were not completely oxidized after 10 h of irradiation, even though naphthalene (6.5×10^{-2} mM) and pentacene were completely oxidized within 4 h and 1 min, respectively (the data for pentacene are not shown here because the concentration could not be determined due to its low solubility). The dicyano acenes could be treated under ambient conditions and are predicted to be more friendly toward device fabrication and encapsulation.

Top-contact field-effect transistors were fabricated by vapor deposition of **DC-NAP** or **DC-PEN** with a thickness of 50 nm onto SiO_2/Si substrates. Contrary to our initial expectation, the dicyano acenes showed ambipolar responses: hole mobility (μ_h) = 2.1×10^{-6} $\text{cm}^2/\text{V}\cdot\text{s}$ and electron mobility (μ_e) = 1.4×10^{-5} $\text{cm}^2/\text{V}\cdot\text{s}$ for **DC-NAP**;

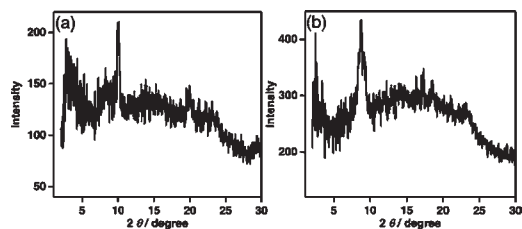
Table 2. OFET Properties of **DC-NAP** and **DC-PEN**

compd	conditions	μ (cm ² /V·s)	on/off	V_{th} (V)
DC-NAP	bare, rt	2.1×10^{-6} (h)	1.3×10^3	-53
		1.4×10^{-5} (e)	9.4×10^0	96
	HMDS, rt	1.7×10^{-5} (h)	1.0×10^4	-53
DC-PEN	bare, rt	1.5×10^{-5} (e)	2.4×10^0	93
		3.1×10^{-4} (h)	2.1×10^2	-46
	HMDS, rt	4.8×10^{-5} (e)	3.0×10^1	16
		3.0×10^{-3} (h)	1.1×10^2	-54
		3.1×10^{-4} (e)	8.2×10^1	-59

$\mu_h = 3.1 \times 10^{-4}$ cm²/V·s and $\mu_e = 4.8 \times 10^{-5}$ cm²/V·s for **DC-PEN**. The results are summarized in Table 2. When HMDS was used as the surfactant, the performance was improved as follows: $\mu_h = 1.7 \times 10^{-5}$ cm²/V·s and $\mu_e = 1.5 \times 10^{-5}$ cm²/V·s for **DC-NAP** and $\mu_h = 3.0 \times 10^{-3}$ cm²/V·s and $\mu_e = 3.1 \times 10^{-4}$ cm²/V·s for **DC-PEN** (Figure 5 and Table 2). The mobilities were not improved by increasing the substrate temperature to 60 °C (Table S2, Supporting Information).

**Figure 5.** Ambipolar OFET output of (a) **DC-NAP** and (b) **DC-PEN** with HMDS as surfactants.

XRD images of dicyano acenes on the surfaces treated with HMDS are shown in Figure 6. A peak was observed at $2\theta = 10.03^\circ$, which corresponded to an interplanar distance of 8.807 Å for **DC-NAP**. This value is close to the molecular length along the long axis (11.4 Å, see Figure 1).

**Figure 6.** XRD images of (a) **DC-NAP** and (b) **DC-PEN** on HMDS.

The **DC-NAP** is expected to stand perpendicular to the surface but tilted about 39°. For **DC-PEN**, a 2θ value of 8.77° (interplanar distance = 10.075 Å) was observed. The weak intensities of the XRD reflection are attributed to the low crystallinity, which might result in the low carrier mobilities. Small grain sizes observed in AFM images of **DC-NAP** and **DC-PEN** on substrates (Figures S3–S6, Supporting Information) agreed with these results.

In conclusion we have synthesized **DC-NAP** and **DC-PEN** as novel and air-stable acene derivatives. These acenes show significantly low HOMO and LUMO levels. The fabricated OFET devices show ambipolar properties with carrier mobilities of 10⁻³ cm²/V·s. The carrier mobilities of **DC-PEN** will be increased by chemical modification such as alkyl-chain introduction to improve the crystallinity.

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Supporting Information Available. Synthetic procedures, optical and electronic properties, OFET outputs, and AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.