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# Dithiophene-Fused Tetracyanonaphthoquinodimethanes (DT-TNAPs): Synthesis and Characterization of $\pi$-Extended Quinoidal Compounds for n-Channel Organic Semiconductor

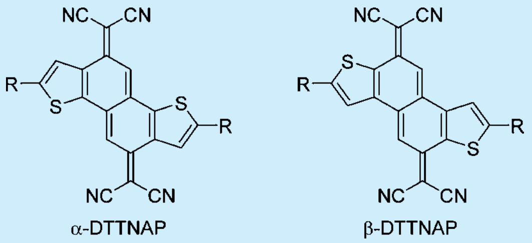
Naoyuki Yanai,[‡,§] Takamichi Mori,[†,‡,§] Shoji Shinamura,[‡] Itaru Osaka,[†] and Kazuo Takimiya*[,†,‡]

[†]Emergent Molecular Function Research Group, RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan

[‡]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

*Supporting Information*

**ABSTRACT:** Dithiophene-fused tetracyanonaphthoquinodimethanes (DTTNAPs) were synthesized and evaluated as n-channel organic semiconductors. DTTNAPs, regardless of isomeric structures and substituents, have low-lying LUMO energy levels (~4.6 eV below the vacuum level), suitable for stable n-channel field-effect transistors (FETs) under ambient conditions. In fact, $\alpha$-DTTNAP derivatives afforded solution-processed FETs showing an electron mobility of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, indicating that DTTNAPs are a potential molecular framework for n-channel organic semiconductors.



Materials evolution is essential for promoting organic electronics. In fact, the performances of organic devices, such as organic field-effect transistors (OFETs) and organic photovoltaics (OPVs), have been significantly enhanced along with the intensive materials research in the past decade.[1] Exploring versatile $\pi$-building blocks that can promote further materials development is thus very important. The acenedithiophene family has been frequently utilized as building blocks to realize superior organic electronic materials. This relies on the following two important molecular factors: one is their $\pi$-extended frameworks with high planarity, which ensures the efficient delocalization of $\pi$-orbitals over the acenedithiophene framework. The other is the existence of two thiophene $\alpha$-positions at both ends of the molecule enabling versatile molecular modification including incorporation into conjugated oligomers and polymers. Indeed, the tricyclic benzodithiophenes (BDTs)[2] and pentacyclic anthradithiophenes (ADTs)[3] have been extensively utilized into a variety of materials, including p- and n-channel molecular semiconductors and semiconducting polymers applicable to OFETs and OPVs.

Until recently, on the other hand, another acenedithiophene member, tetracyclic naphthodithiophenes (NDTs), has not been exploited, because of their poor accessibility. However, recent synthetic endeavors have realized practical access to NDTs,[4] and then the NDT derivatives were examined as molecular semiconductors, conjugated oligomers, and semiconducting polymers for high performance OFETs and OPVs.[5] All of these NDT-based materials so far examined are p-channel organic semiconductors, since the electronic structure of NDTs enables a high-lying HOMO energy level ($E_{\mathrm{HOMO}}$) suitable for p-channel organic semiconductors rather than the low-lying LUMO energy level ($E_{\mathrm{LUMO}}$) for n-channel. For the development of n-channel organic semiconductors by lowering $E_{\mathrm{LUMO}}$ and maintaining the same molecular framework, introduction of a quinoidal structure with strong electron withdrawing terminal groups, such as dicyano-, ((alkyloxy)carbonyl)cyano-, or (acyl)cyano-methylene termini, is one of the most reliable ways.[6] We demonstrate here the first example of NDT-based electron deficient molecules, isomeric dithiophene-fused tetracyanonaphthoquinodimethanes ($\alpha$- and $\beta$- DTTNAPs, Figure 1), as a potential structure for n-channel organic semiconductors, by taking advantage of the selective functionalization of the angular-shaped NDTs.[7]

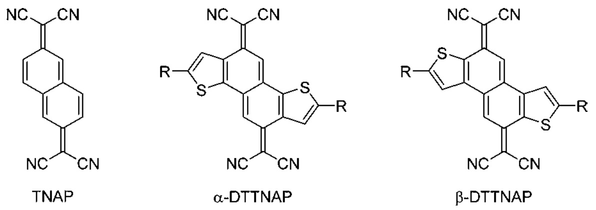


**Figure 1.** Structures of TNAP and $\alpha$- and $\beta$-DTTNAPs.

Depicted in Scheme 1 is the synthesis of $\alpha$- and $\beta$-DTTNAPs. Regioselective bromination of 5- and 10-positions on naphtho[1,2-*b*:5,6-*b*′]- and naphtho[2,1-*b*:6,5-*b*′]-dithiophenes via Ir-catalyzed borylation and the following reaction with CuBr afforded the precursors,[7] which can readily be converted into the corresponding bis(dicyanomethyl) derivatives via the Takahashi reaction,[8] which were further oxidized to produce DTTNAPs in moderate yields. It is interesting to note that their solubilities are dependent on not only the

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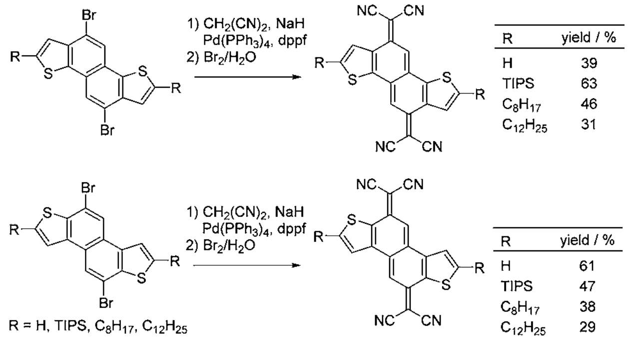
**Scheme 1. Synthesis of α- and β- DTTNAPs**



substituents at the thiophene α-positions but also the isomeric structure according to the direction of the thiophene rings. α-DTTNAPs with the tri(isopropylsilyl) (TIPS)- or long alkyl groups show good solubility (>3 g $L^{-1}$ in chloroform at 60 °C), whereas the solubilities of β-DTTNAPs are, regardless of the substituents, relatively lower (∼1 g $L^{-1}$ under the identical conditions, Table S1), limiting the deposition of their thin films from solution (vide infra).

Single crystals of TIPS-substituted α- and β-DTTNAPs with suitable quality for the X-ray structural analysis were grown by recrystallization from chloroform. As expected from the canonical structures, both molecules show clear bond length alternation that represents the naphthoquinoidal structure (Figure S1). On the other hand, there exists noticeable distortion in the molecular structure of TIPS-α-DTTNAP; the dicyanomethylene moieties in TIPS-α-DTTNAP sit slightly away from the thiophene moieties along with relatively large dihedral angles defined by the NDT core and the dicyanomethylene moiety (ca. 9.2°). This can be caused by the close proximity of one of the cyano groups and the β-hydrogen atom in the thiophene. Since such molecular distortion is much smaller in TIPS-β-DTTNAP, the difference in their solubility could be related to this structural factor.

Electrochemical and optical evaluations of DTTNAPs in solution afford estimation of their electronic structures. From the reduction onset in cyclic voltammograms (Figure 2a), $E_{LUMO}$ values of DTTNAPs, regardless of the isomers and substituents at the thiophene α-positions, are estimated to be 4.6 eV below the vacuum level, which is almost the same with that of TNAP (Figure 3, Table S2).[9] This can be qualitatively explained by the electronic structure of LUMOs; as demonstrated in Figure 3, the LUMOs of both α- and β-DTTNAPs localized on the TNAP moiety, not steeping out to the thiophene moieties, indicating that the annulation of thiophenes affords negligible perturbation in the electronic structure of LUMO. From the absorption onset (Figure 2b),[10] the HOMO−LUMO energy gap ($E_g$) can be estimated to be 2.2 eV for DTTNAPs and 2.4 eV for TNAP, respectively, implying similar $E_{HOMO}$ values for DTTNAPs and TNAP (Figure 3). This can be rationalized by the electronic structures of HOMOs calculated by the DFT methods, indicating that the major conjugation path, regardless of the direction of the annulated thiophene rings, is on the TNAP moiety.

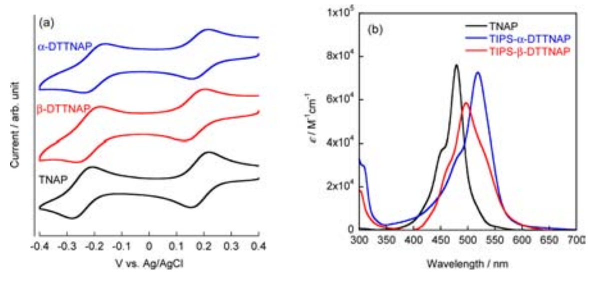


**Figure 2.** Cyclic voltammograms (V vs Ag/AgCl in dichloromethane containing 0.1 M tetarabutyl ammonium hexafluorophospate, scan rate: 100 mV $s^{-1}$) of α- and β-DTTNAPs and TNAP (a) and absorption spectra in dichloromethane of α- and β-TIPS-DTTNAPs and TNAP (b).

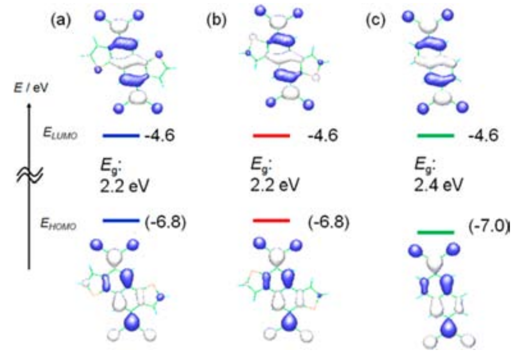


**Figure 3.** Electronic structure of DTTNNAPs and TNAP. The $E_{HOMO}$s in parentheses are estimated from the electrochemical $E_{LUMO}$ and optical $E_g$. The spacial distribution of HOMO and LUMO are calculated by DFT methods at the B3LYP/6-31g(d) level.

Parent α- and β-DTTNAP can afford uniform thin films on $Si/SiO_2$ substrates by vapor deposition, and as expected from their low-lying $E_{LUMO}$s, the films acted as an n-channel semiconductor with field-effect electron mobilities on the order of $10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$. However, the devices did not show a clear off-state, similar to the case reported for the TNAP-based[9] and related dicyanomethylene-terminated quinoidal benzo[1,2-*b*:4,5-*b*′]dithiophene-based OFETs (Figure S5).[11] Thin films of $C_8$- and $C_{12}$-α-DTTNAP can be deposited by spin-coating from 0.2 wt % chloroform solution. However, the quality of the thin film deposited on $Si/SiO_2$ substrates, especially ones with a self-assembled monolayer (SAM)-modified surface, was poor, and thus, the reproducibility of device performances was not very good. Nevertheless, the devices with a typical top-contact, bottom-gate configuration on the $Si/SiO_2$ substrates showed n-channel transistor responses under ambient conditions. The extracted mobilities were on the order of $10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$, and the maximum electron mobility was $2.4 \times 10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$ with an on/off ratio of $10^3$ for $C_8$-α-DTTNAP (Table S3 and Figure S6). In contrast, deposition of thin films on glass substrates was more reproducible, and with the thin film on the glass substrate, FET devices with a top-gate, bottom-contact (TGBC) configuration were fabricated and evaluated (Figure 4 and Table 1). As expected from better reproducibility of the thin film deposition, the yield ratio of OFETs was improved for the TGBC devices, though the overall device characteristics were only slightly improved, with a mobility of up to $4.6 \times 10^{-3}$ $cm^2$ $V^{-1}$ $s^{-1}$ with an on/off ratio of $10^5$ for $C_8$-α-DTTNAP-based OFETs.

The moderate mobilities of α-DTTNAP-based devices can be understood by relatively poor molecular ordering as testified by X-ray diffraction (XRD) patterns (Figure 5). The as-spun thin film of $C_8$-α-DTTNAP showed a major crystalline peak at 4.04° with a minor peak at 5.08°, indicative of the coexistence

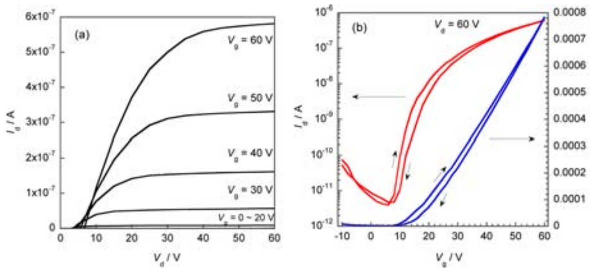


**Figure 4.** Output (a) and transfer characteristics (b) of $C_8$-$\alpha$-DTTNAP-baed devices annealed at 150 °C.

**Table 1. FET Characteristics of $\alpha$-DTTNAP-Based Devices with a Top-Gate, Bottom-Contact (TGBC) Configuration**[a]

| compound | anneal/°C | $\mu_{av}{}^{b}(\mu_{max})$/cm$^2$ V$^{-1}$ s$^{-1}$ | $I_{on}/I_{off}$ | $V_{th}$/V |
|---|---|---|---|---|
| $C_8$-$\alpha$-DTTNAP | – | $1.2 \times 10^{-3}$ ($1.5 \times 10^{-3}$) | $10^3$ | 17 |
| | 50 | $1.4 \times 10^{-3}$ ($1.9 \times 10^{-3}$) | $10^3$ | 18 |
| | 100 | $1.9 \times 10^{-3}$ ($3.3 \times 10^{-3}$) | $10^4$ | 15 |
| | 150 | $3.2 \times 10^{-3}$ ($4.6 \times 10^{-3}$) | $10^5$ | 12 |
| $C_{12}$-$\alpha$-DTTNAP | – | $7.4 \times 10^{-4}$ ($8.6 \times 10^{-4}$) | $10^3$ | 2.8 |
| | 50 | $8.7 \times 10^{-4}$ ($1.0 \times 10^{-3}$) | $10^3$ | 3.8 |
| | 100 | $1.3 \times 10^{-3}$ ($1.7 \times 10^{-3}$) | $10^3$ | 2.8 |
| | 150 | $1.4 \times 10^{-3}$ ($2.7 \times 10^{-3}$) | $10^3$ | 5.9 |

[a] CYTOP was used as the gate dielectric. [b] From more than five devices.

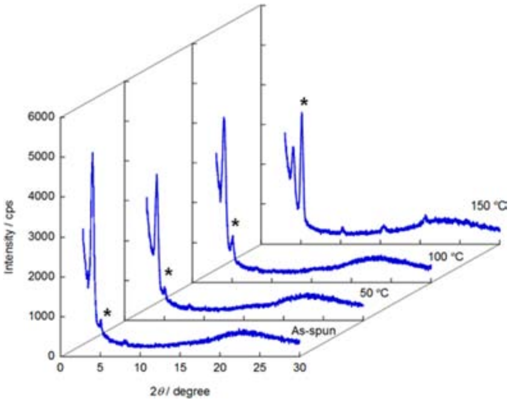


**Figure 5.** XRD patterns of $C_8$-$\alpha$-DTTNAP thin film annealed at different temperatures on the glass substrate.

of two crystalline phases. Upon thermal annealing, the latter peak (peaks with asterisk) is intensified with higher-order peaks, whereas the former is weakened. By correlation of the FET mobilities and the XRD patterns depending on the annealing temperatures (Table 1, Figure 5), it is speculated that the latter crystalline phase must show higher mobility than the former. However, even in the thin film annealed at 150 °C, the peak at 4.04° still remains, and a much higher annealing temperature degraded the thin film, indicating that improvement of molecular ordering and phase control by thermal annealing has certain limitations.

In summary, we have synthesized dithiophene-fused tetracyanonaphthoquinodimethanes (DT-TNAPs) and evaluated them as n-channel organic semiconductors. DT-TNAPs have low-lying $E_{LUMO}$ values (4.6 eV below the vacuum level) regardless of isomeric structures and substituents, enabling stable operation of n-channel OFETs under ambient conditions. In fact, $\alpha$-DTTNAP derivatives afford solution-processed FETs showing a mobility of $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, indicating that DTTNAPs are a potential framework for n-type organic semiconductors. On the other hand, poor crystallinity with a less ordered structure in the thin film state is supposed to be one of the reasons for the moderate device characteristics. Improvement of microstructures by molecular modification will be a promising measure. To this end, utilization of easy derivatization at the thiophene $\alpha$-positions, new molecular designs, and syntheses is now underway in our group.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, NMR spectra, CIF for TIPS-$\alpha$- and $\beta$-DTTNAP. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: takimiya@riken.jp.

### Author Contributions

[§] These authors contributed equally.

### Notes

The authors declare no competing financial interest.

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