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Thieno[3,4-*c*]pyrrole-incorporated quinoidal terthiophene with dicyanomethylene termini: synthesis, characterization, and redox properties

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ABSTRACT

Synthesis, characterization, molecular structure, and redox properties of a new quinoidal terthiophene incorporated with a thieno[3,4-*c*]pyrrole moiety (**5**) are described. Although an electrochemical reduction of **5** formally produces the non-classical thieno[3,4-*c*]pyrrole moiety, **5** showed a reversible reduction wave on cyclic voltammogram, indicating that the thieno[3,4-*c*]pyrrole moiety can be stabilized by delocalized 10π-conjugated system in the dianion state of **5**. However, the reduction potential was largely affected by incorporation of the thieno[3,4-*c*]pyrrole and shifted cathodically by 0.4 V compared to that of the parent quinodial terthiophene (**1**).

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7,7,8,8-Tetracycanoquinodimethane (TCNQ) and its related compounds have long been known as superior electron-accepting molecules and widely studied in the field of organic charge-transfer complexes.[1] Owing to their low-lying LUMO energy levels, the TCNQ-type compounds have recently been focused as n-channel organic semiconductors.[2] In fact, dicyanomethylene-substituted quinoidal oligothiophenes (e.g., **1**)[3] are one of the representative classes of n-channel organic semiconductors, and vacuum-deposited thin film of the terthiophene derivative with two butyl substituents (**2**) gave a superior n-channel organic field-effect transistors (OFETs) (Fig. 1).[4] Another interesting compound in this class is cyclopentene-annulated terthienoquinoidal (**3**) that affords air-stable, solution-processed n-channel FETs with electron mobility of 0.16 cm^2/Vs.[5] Considering the fact that the unsubstituted terthienoquinodal (**1**) is rather inferior as the active semiconducting material in the OFET devices,[6] the thienoquinoidal molecules **2** and **3** are good examples showing the importance of tuning of molecular structures enabling appropriate molecular ordering in the thin film state.

From this viewpoint, we have pursued new interesting systems by modifying the molecular structure of **1** and designed a quinoidal terthiophene with a similar structural motif to **3** employing *N*-octyldihydropyrrole moiety annulated on the central thiophene ring (**4**). The *n*-octyl group in **4** can act as a solubilizing group, but the *N*-octyldihydropyrrole moiety is sterically less hindered compared to the cyclopentane-based solubilizing moiety in **3**, facilitating a better planarity and hence strong intermolecular interaction in the solid state.

We thus attempted to synthesize **4**, but it turned out that **4** is not isolable: instead, its dehydrogenated compound, that is, a thieno[3,4-*c*]pyrrole-1,3-diylidene-incorporated terthienoquinoidal (**5**) was reproducibly obtained (Fig. 1). Compound **5** is interesting not only as a new class of organic semiconductor but also as a rare π-system that contains the thieno[3,4-*c*]pyrrole-1,3-diylidene moiety, which, upon reduction, produces a non-classical thiophene ring system, thieno[3,4-*c*]pyrrole moiety.[7] Since this kind of terthienoquinoidal with thieno[3,4-*c*]pyrrole moiety has been so far unknown, it is very interesting to address how the moiety affects the molecular properties, in particular its redox properties. In this Letter,

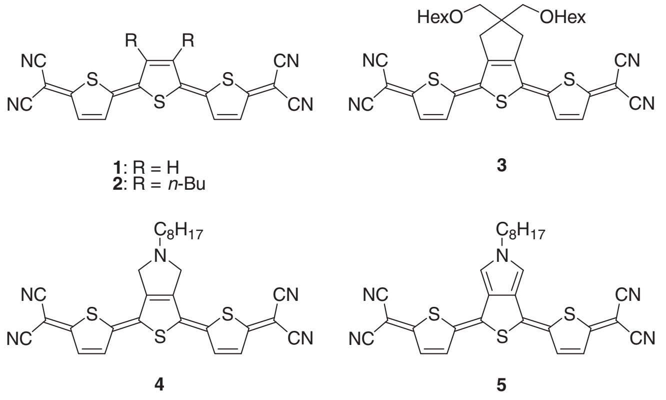

Figure 1. Molecular structures of quinoidal terthiophenes.

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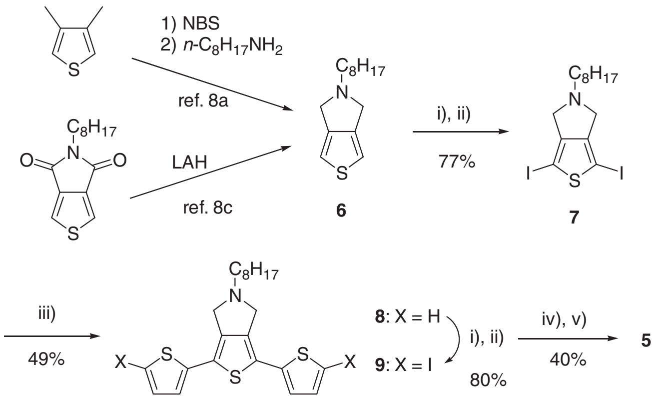


Scheme 1. Synthesis of **5**. Reagents and conditions: (i) *n*-BuLi; (ii) *n*-$C_6F_{13}I$; (iii) $Pd(PPh_3)_4$, 2-(tributylstannyl)thiophene (twofold); (iv) $Pd(PPh_3)_4$, CH_2CN_2, NaH; (v) HCl aq, air oxidation.

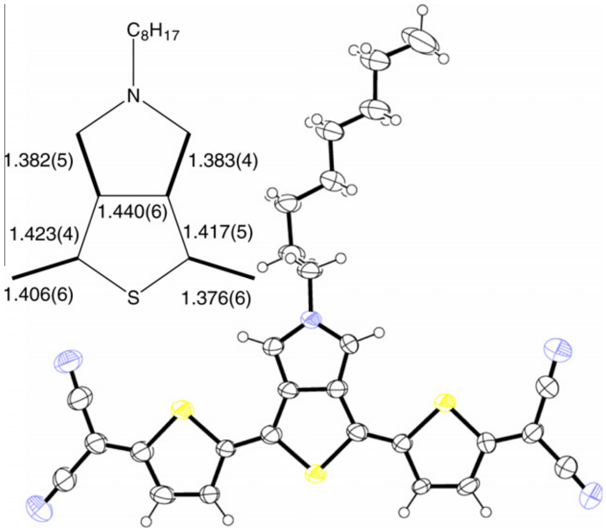
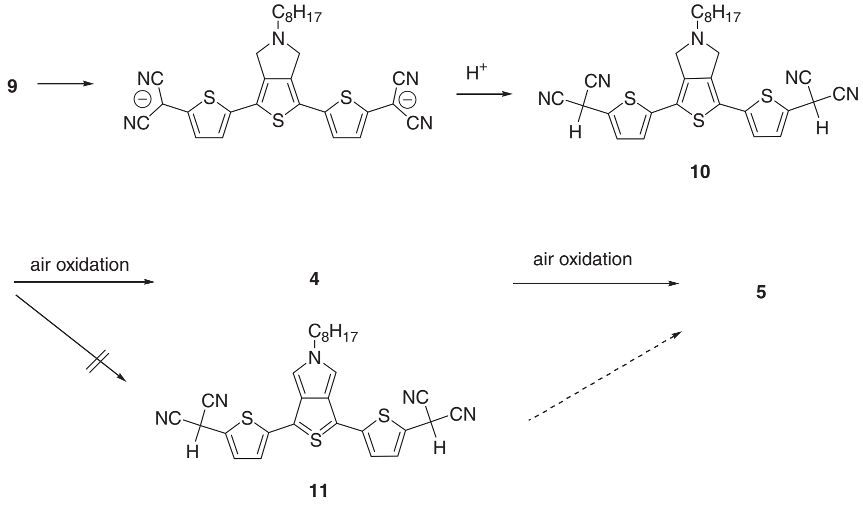


Figure 2. ORTEP drawing of **5** (DMF, the crystallization solvent, is omitted for clarity), and selected bond lengths in the central thieno[3,4-*c*]pyrrole moiety, where bonds represented with the bold face have significant double bond character.

we report the synthesis, molecular structure, and physicochemical characterization of a new pyrrole-annulated terthienoquinoidal compound (**5**).

In our initial synthetic attempts for **4**, 5-octyl-5,6-dihydro-4*H*-thieno[3,4-*c*]pyrrole (**6**) was selected as a starting material (Scheme 1), which was readily synthesized according to the reported procedures.[8] Although electrophilic bromination of **6** using *N*-bromosuccinimide or bromine, or lithiation/halogenation with *n*-BuLi/iodine or *n*-BuLi/1,2-dibromo-1,1,2,2-tetrachloroethane did not afford halogenated **6**, the diiodo derivative (**7**) can be prepared via lithiation of **6** with *n*-BuLi followed by a reaction with perfluorohexyl iodide in 77% isolated yield. Then, the palladium-catalyzed Stille cross-coupling reaction of **7** with 2-tributylstannylthiophene afforded the terthiophene derivative with dihydropyrrolo ring at the central thiophene (**8**) in 49% yield. Iodination of **8** using similar reaction conditions to those of **6** smoothly afforded **9** (80% isolated yield). Introduction of the dicyanomethyl moiety followed by the air-mediated oxidation was carried out using dicyanomethanoide anion in the presence of the palladium (0) catalyst.[9] Although the reaction gave a deep green colored product reproducibly (40% isolated yield), which seems to be the desired compound (**4**), its mass spectrum showed a molecular ion peak (M^+) at $m/z = 525$, smaller than the expected M^+ of **4** ($m/z = 527$) by two. Furthermore, ^1H NMR spectra of the product showed no peak at around 4.0 ppm assignable to the dihydropyrrole moiety (see Supplementary data). Instead, a singlet peak at around 7.2 ppm was detected, reasonably assignable to a pyrrole moiety rather than the dihydropyrrole moiety. This spectroscopic characterization strongly suggested that the product must be **5** with the thieno[3,4-*c*]pyrrole-1,3-diylidene moiety at the central ring (Scheme 1). The unambiguous structural determination was achieved by the X-ray crystallographic analysis.[10,11] As shown in Figure 2, the bond length alternation clearly supports that the nitrogen-containing five-membered ring fused at the central thiophene moiety is pyrrole-like, rather than dihydropyrrole.

Scheme 2 shows a speculated reaction path to **5**. An ordinary substitution reaction of **9** with dicyanomethanoid anions gave the dianion intermediate, which is then protonated to give **10**. Under the ambient air condition, **10** is first oxidized to **4**, rather than to **11** with the non-classical thieno[3,4-*c*]pyrrole moiety. Since **4** contains a dihydoropyrrole structure and further oxidation does not produce the non-classical thieno[3,4-*c*]pyrrole moiety, **4** can be smoothly oxidized to give **5** with the thieno[3,4-*c*]pyrrole-1,3-diylidene moiety.



Scheme 2. Plausible reaction path to **5** via **4**.

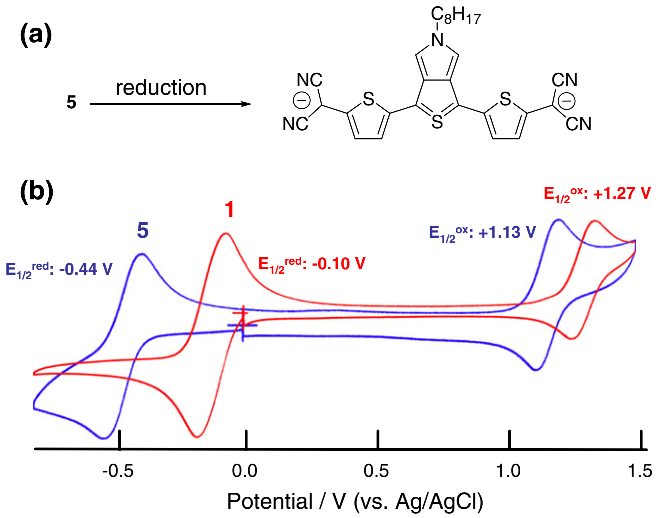


Figure 3. (a) Dianion of **5** with the non-classical thieno[3,4-*c*]pyrrole moiety and (b) cyclic voltammogram of **5** together with **1** (solvent: PhCN, supporting electrolyte: *n*-Bu$_4$NPF$_6$, scan rate: 100 mV/s, counter and working electrodes: Pt).

Although it was not the initial target, **5** is an interesting compound as a new redox active π-system, because the incorporated thieno[3,4-*c*]pyrrole-1,3-diylidene moiety can reproduce the non-classical thieno[3,4-*c*]pyrrole moiety upon electrochemical reduction (Fig. 3a). This poses an interesting question as to how such structural contribution affects its redox properties and furthermore, whether the reduced state of **5** is stable or not.

Figure 3b shows cyclic voltammogram of **5** together with the parent quinoidal terthiophene (**1**). The electrochemical reduction of **5** occurs at a lower potential ($E_{1/2}^{red}$: -0.44 V vs Ag/AgCl) than that of **1** ($E_{1/2}^{red}$: -0.10 V vs Ag/AgCl) by 0.34 V, indicating the significantly reduced electron-accepting nature of **5**. In contrast, the oxidation potential of **5** ($E_{1/2}^{ox}$: +1.13 V) shifts cathodically only by 0.14 V compared to that of **1** ($E_{1/2}^{ox}$: +1.27 V). Larger cathodic shift of the reduction potential compared to that of the oxidation potential could be explained as follows: the inductive effect from the electron-donating pyrrole moiety causes the cathodic shift in both the oxidation and reduction processes. On the other hand, reduction of **5** produces energetically less-favorable non-classical thieno[3,4-*c*]pyrrole moiety, which shifts further the reduction potential cathodically. In addition to these potential shifts, the reduction process occurred reversibly, indicating that the dianion state of **5** is electrochemically stable, which can be rationalized by taking into account the delocalized 10π-conjugated system at the thieno[3,4-*c*]pyrrole moiety contributed by dipolar ylide forms already mentioned by Cava et al. as depicted in Figure 4.[7]

In summary, we have unexpectedly isolated the new quinoidal terthiophene with a thieno[3,4-*c*]pyrrole moiety (**5**). Perturbation of the annulated pyrrole moiety is quite significant to the redox properties of the quinoidal terthiophene, in particular reduction potential shift is very large, although the reversibility of the reduction process is not affected. Therefore, it is expected that this kind of molecular modification will be a useful tool for controlling the electron-accepting and/or electron-donating nature as well as the HOMO–LUMO energy gap of the thienoquinoidal systems. Preliminary trials using **5** as a solution-processable semiconducting material were not successful so far, owing to its poor solubility in ordinary organic solvents (e.g., 0.1 g/L in chloroform at rt). Therefore, further molecular modification to enhance solubility by changing the alkyl group on the nitrogen atom is now underway.

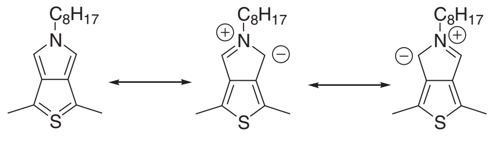


Figure 4. Stabilization of non-classical thieno[3,4-*c*] moiety.

Acknowledgments

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Supplementary data

Supplementary data (synthetic procedures, crystallographic information file (CIF), and UV–vis spectra for **5**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.052.

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10. Single crystals of **5** suitable for X-ray structural analysis were obtained by careful recrystallization from DMF. The X-ray crystal structure analysis was made on a Rigaku DSC imaging plate system by using Si-monochromated synchrotron ($\lambda = 1.00000$ Å) at beam line BL-8B of Photon Factory (PF), High Energy Accelerator Research Organization (KEK). Crystallographic data for **5** DMF: $C_{31}H_{30}N_6OS_3$ (598.82), black needles, $0.30 \times 0.05 \times 0.02$ mm^3, *Triclinic*, space group, $P\bar{1}$ (#2), $a = 8.1389(5)$, $b = 11.0698(6)$, $c = 18.102(3)$ Å, $\alpha = 76.233(6)$, $\beta = 78.218(8)$, $\gamma = 86.925(4)°$, $V = 1550.6(3)$ Å^3, $Z = 2$, $R = 0.1043$ for 3180 observed reflections ($I > 2\sigma(I)$) and 370 variable parameters, $wR^2 = 0.2935$ for all data.
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