

Biradical Character of Linear π -Conjugated Oligomer Dications Composed of Thiophene, Pyrrole, and Methylthio End-Capping Units

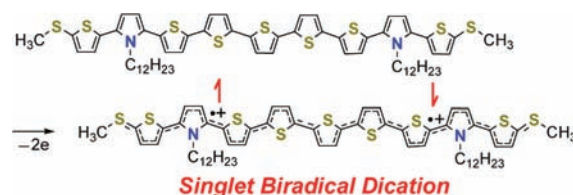
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ABSTRACT



Combined DFT calculations and UV–vis–NIR, ESR, and SQUID measurements revealed that the ground-state electronic structure of a linear π -conjugated oligomer dication composed of two pyrrole and six or seven thiophene rings and methylthio end-capping units is dominated by a singlet biradical character.

Cationic species of α -linked linear oligothiophenes have been intensively investigated as models of p-doped states of conducting polythiophenes.¹ In particular, oligothiophene dications are key species to understand the electronic structure of polythiophenes at high p-doping levels. Recent theoretical studies demonstrated that oligothiophene dications composed of four (TDB3P86–30%)² or six (B3LYP)^{3,4} thiophene rings have a singlet biradical character, whereas a previous experimental study using absorption spectroscopy in solution suggested that much longer oligomer length such as the dodecamer is necessary for the dication to show biradical character.⁵ Recently, however, it was pointed out that the absorption spectrum of the sterically unhindered

dodecithiophene dication, which showed two broad absorption bands assigned as an intrachain polaron pair (i.e., biradical dication),⁵ was totally different from that of a sterically hindered dodecithiophene dication, which showed only one broad absorption band.⁶ The discrepancy between the sterically unhindered and hindered oligomers may be brought about by the presence and absence of an intermolecular π – π interaction, but the cause remains unclear. This ambiguity stems partly from lack of information about solid-state properties of oligothiophene dications.

We are also interested in the electronic structure of cationic oligothiophenes and have reported the synthesis and properties of cationic oligothiophenes stabilized by the annelation with bicyclo[2.2.2]octene units.^{7,8} Among these oligomers, X-ray analysis of sexithiophene dication salts unambiguously

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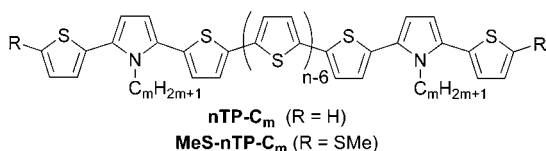
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demonstrated that an intermolecular π - π interaction is inhibited by the rigid bicyclo[2.2.2]octene frameworks in the solid state,^{8c} and a comparison between calculated and observed absorption spectra suggested that the oligomer dication with six or more rings have a singlet biradical character.^{8a} These results prompted us to investigate the solid state properties of sterically unhindered linear oligomer dications. For this purpose, we chose thiophene-pyrrole mixed oligomers end-capped with methylthio substituents (**MeS-nTP-C_m**). Both the replacement of two thiophene rings with pyrrole rings⁹ and the end-capping with thio groups¹⁰ are expected to be effective for stabilization of cationic oligomers without significant change in the electronic structures as linear oligomers composed of five-membered heteroaromatics. Here we report the biradical character of such oligomer dications.



The effects of both replacement with pyrrole rings and methylthio end-capping for the biradical character in comparison with α -linked linear oligothiophene dications (**nT²⁺**) were assessed first by DFT calculations at the B3LYP/6-31G(d) level. In the case of **nT²⁺**, the energy of unrestricted (U) wave function (UB3LYP/6-31G(d)) of open-shell singlet configuration (singlet biradical) becomes lower than that of the restricted (R) wave function (RB3LYP/6-31G(d)) of closed-shell configuration when $n > 6$.^{3,4} The energy differences ($\Delta E_{(R-U)} = E_{(RB3LYP)} - E_{(UB3LYP)}$) of **6T²⁺**, **7T²⁺**, **8T²⁺**, and **9T²⁺** are 0.2, 0.8, 1.6, and 2.4 kcal mol⁻¹,³ respectively, indicating that the relative stability of the open-shell singlet state increases with increasing chain length.

Similarly, for **nTP-C₁²⁺**, the values of $\Delta E_{(R-U)}$ (Table 1) were calculated to be 0.5 ($n = 6$), 1.4 ($n = 7$), 2.5 ($n = 8$), and 3.3 kcal mol⁻¹ ($n = 9$). From the comparison of $\Delta E_{(R-U)}$ between **nT²⁺** and **nTP-C₁²⁺**, it was found that the replacement with two *N*-methylpyrrole rings causes larger $\Delta E_{(R-U)}$. Furthermore, when the $\Delta E_{(R-U)}$ values of **nTP-C₁²⁺** and **MeS-nTP-C₁²⁺** were compared, it was shown that the end-capping with methylthio units further stabilizes singlet biradical state by 1.1–1.4 kcal mol⁻¹ owing to the π -extension with the end-capping thio substituents.

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Table 1. Relative Energies (in kcal mol⁻¹) for **nTP-C₁²⁺** and **MeS-nTP-C₁²⁺** in Spin-Restricted Singlet (R), Spin-Unrestricted Singlet (U), and Triplet (T) States at the B3LYP/6-31G(d) Level

compd	$\Delta E_{(R-U)}$	$\Delta E_{(T-U)}$	$\Delta E_{(T-R)}$
6TP-C₁²⁺	0.5	4.8	4.3
7TP-C₁²⁺	1.4	3.1	1.7
8TP-C₁²⁺	2.5	2.1	-0.4
9TP-C₁²⁺	3.3	1.5	-1.8
MeS-6TP-C₁²⁺	1.7	2.6	0.9
MeS-7TP-C₁²⁺	2.8	1.8	-1.0
MeS-8TP-C₁²⁺	3.7	1.2	-2.5
MeS-9TP-C₁²⁺	4.4	0.9	-3.5

On the other hand, the energy differences between the singlet biradical (U) and triplet (T) states ($\Delta E_{(T-U)}$) of **nTP-C₁²⁺** and **MeS-nTP-C₁²⁺** were also positive and decreased with increasing chain length and methylthio end-capping. These results indicate that the singlet biradical state is lower in energy than the triplet state and that both types of π -extensions lead to a decrease of the energy difference. In other words, the exchange interaction between the spins of a radical cation pair decreases with expanding the π -system. Similar chain length dependence of $\Delta E_{(T-U)}$ was also observed for **nT²⁺**.³

Concerning the electronic structure of the singlet biradicals (U), the spin distributions of **8T²⁺**, **8TP-C₁²⁺**, and **MeS-nTP-C₁²⁺** are similar and delocalized over the whole π -systems (Figure 1 and Figure S1, Supporting Information).

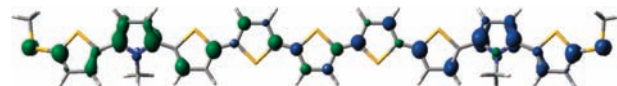


Figure 1. Spin distribution of the singlet biradical state (U) of **MeS-9TP-C₁²⁺**.

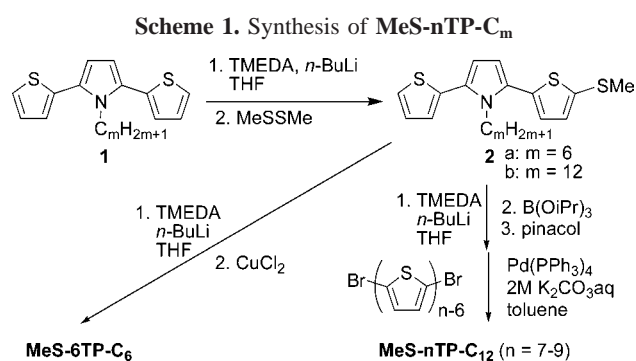
The S^2 values of the singlet biradical states of **MeS-nTP-C₁²⁺** increase with increasing chain length as observed in **nT²⁺**,³ and the values of **MeS-nTP-C₁²⁺** (0.76–0.97) are higher than those of **nT²⁺** with same chain length (Table S1, Supporting Information). Also the biradical indexes of **MeS-nTP-C₁²⁺** ($n = 6$ –9) estimated by NOON (natural orbital occupation number) analysis¹¹ at the B3LYP/6-31G(d) level were calculated to be 48%, 59%, 66%, and 71%, respectively, and the biradical index of **MeS-8TP-C₁²⁺** (66%) was shown to be higher than that of **8T²⁺** (46%).^{8a} Thus, the π -extensions by elongation of chain length and by methylthio end-capping and the replacement with pyrrole ring were shown to enhance the biradical character of linear oligomer dications.

In the optimized structures of **MeS-nTP-C₁²⁺**, the pattern of carbon-carbon bond length alternation (BLA) of the singlet biradical states becomes more similar to that of triplet

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states rather than that of closed-shell singlet states, as the chain length increases (see Figure S2, Supporting Information). For $n = 8$ and 9 , the structural difference between the open- and closed-shell states appears especially in the central thiophene rings, where the open-shell states have an “aromatic” BLA pattern^{3,12} in contrast to a quinoid BLA pattern for the closed-shell states, reflecting that a radical cation pair tends to separate each other in the longer oligomers. These results correlate with the decrease of $\Delta E_{(T-U)}$ and the increase of singlet biradical character with increasing chain length.

For the synthesis of **MeS-nTP-C_m**, thiophene–pyrrole trimer **1**¹³ prepared by the Paal–Knorr method was monolithiated, followed by the reaction with dimethyl disulfide to give **2** (Scheme 1). Then, homocoupling of **2a** was

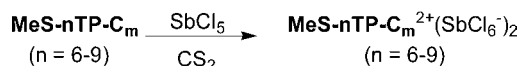


conducted for **MeS-6TP-C₆**, while Suzuki–Miyaura coupling was performed for **MeS-nTP-C₁₂** ($n = 7–9$).

Cyclic voltammetry of **MeS-nTP-C_m** showed reversible one-step two-electron oxidation processes (Figure S3, Supporting Information), indicating that the generated dications are stable in the measurement conditions with no apparent on-site Coulombic repulsion. In the case of **8TP-C₁₂** without the methylthio end-capping groups, the electropolymerization was observed in the same measurement conditions, whereas such electropolymerization was not observed for **6TP-C₁₂** (Figure S4, Supporting Information). Thus, the methylthio units play a critical role in the reversibility of the longer oligomers, and no occurrence of electropolymerization for **6TP-C₁₂** suggests that biradical character presents only in the longer oligomer dications. On the other hand, the oxidation potentials of **MeS-6TP-C₆** (0.16 V vs Fc/Fc⁺) and **MeS-nTP-C₁₂** ($n = 7$: 0.15 V; $n = 8$: 0.14 V; $n = 9$: 0.12 V) are similar. Thus, the increase in oligomer lengths does not greatly affect the oxidation potentials.

Reflecting these reversible two-electron oxidations at relatively lower oxidation potentials, stable dark-colored precipitates were obtained when the oligomers in CS₂ were oxidized with ca. 2.5 equiv of SbCl₅. Elemental analysis of these precipitates suggest that they are dication salts of **MeS-nTP-C_m**²⁺(SbCl₆[−])₂ ($n = 6–9$) (Scheme 2), although they appear to be contaminated with some paramagnetic impurity as described below.

Scheme 2. Synthesis of MeS-nTP-C_m²⁺(SbCl₆[−])₂



As shown in Figure 2, the absorption spectra of **MeS-nTP-C_m**²⁺ ($n = 6, 7$) generated with SbCl₅ in CH₂Cl₂ showed one strong absorption band at near-IR regions ($n = 6$: 965 nm (log $\epsilon = 5.1$); $n = 7$: 1093 nm (5.1)) together with weak absorption bands at visible regions. In contrast,

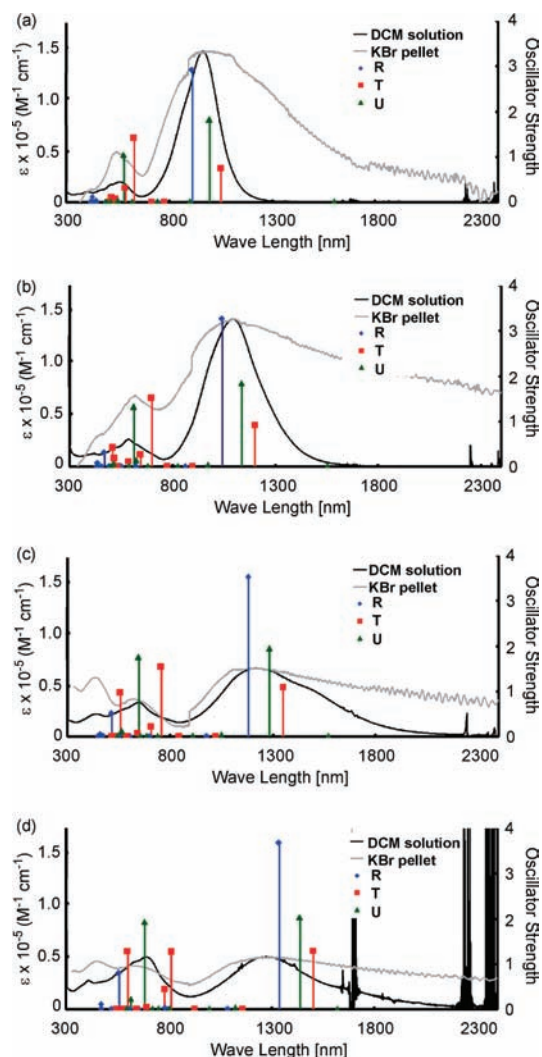


Figure 2. UV–vis–NIR spectra of **MeS-nTP-C_m²⁺(SbCl₆[−])₂** ((a) $n = 6$, (b) $n = 7$, (c) $n = 8$, and (d) $n = 9$) in CH₂Cl₂ (DCM) solution ($10^{-4} - 10^{-5}$ M) and in KBr pellet. The results of TD-DFT calculations of spin-restricted singlet (R), spin-unrestricted singlet (U), and triplet (T) states at the B3LYP/6-31G(d) level are also depicted as bar graphs. (The intensities of the longest absorption maxima observed in the solid state are normalized to those observed in solution, while the heights of the calculated spectra reflect the calculated oscillator strengths.) See Table S2 (Supporting Information) for the values of absorption maxima, absorption coefficients, and oscillator strengths.

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two broad absorption bands were observed for the longer oligomer **MeS-nTP-C₁₂²⁺** ($n = 8$: 1212 nm ($\log \epsilon = 4.8$), 648 nm (4.5); $n = 9$: 1275 nm ($\log \epsilon = 4.7$), 692 nm (4.7)). To consider the difference in the spectral patterns, TD-DFT calculations (B3LYP/6-31G(d)) were performed for closed-shell singlet (R), open-shell singlet (U), and triplet (T) of **MeS-nTP-C₁²⁺**, and the results are depicted in Figure 2 as bar graphs. According to the calculations, the closed-shell singlet state has one strong absorption band, and the oscillator strength increases with increasing chain length. On the other hand, open-shell singlet and triplet were predicted to have two or three bands with oscillator strengths similar to each other. In addition, the oscillator strengths of open-shell states are about half of the corresponding closed singlet state, as observed in the apparent decrease of absorption coefficients from **MeS-7TP-C₁₂²⁺** to **MeS-8TP-C₁₂²⁺**. Thus, the observed spectra of **MeS-nTP-C_m²⁺** ($n = 6, 7$) appear to be consistent with the calculated spectra of closed-shell singlet state, suggesting that these dications are dominated by a closed-shell nature. On the other hand, the observed spectra of **MeS-nTP-C₁₂²⁺** ($n = 8, 9$) are considered to be assigned as open-shell states. The gradual decrease of the longest absorption band with increasing chain length may indicate that the both closed- and open-shell singlet states coexist as isomers in **MeS-7TP-C₁₂²⁺** and **MeS-8TP-C₁₂²⁺**.

Solid-state absorption spectra of **MeS-nTP-C_m²⁺**(SbCl₆⁻)₂ in a KBr pellet were also measured (Figure 2), and it was found that the absorption maxima for all dications are essentially the same as those in the dilute solution. If there is a bonding intermolecular interaction in the solid state as observed in the radical cation π -dimers^{8b,14} and phenalenyl-based singlet biradicals,¹⁵ the absorption maxima are expected to shift. Therefore, the π -dimer formation between dication as mentioned in previous studies⁶ seems not to take place in the solid states. ESR spectra of the solids of **MeS-nTP-C_m²⁺**(SbCl₆⁻)₂ showed weak broad signals (Figure S5, Supporting Information), and the estimated radical concentrations (external standards with DPPH) were 0.4%, 4%, 12%, and 12% for $n = 6-9$, respectively.

On the other hand, the temperature dependence of susceptibility (χ_M : molar susceptibility) of **MeS-9TP-C₁₂²⁺**(SbCl₆⁻)₂ measured by SQUID revealed that a $\chi_M T$ vs T plot (Figure S6, Supporting Information) is almost flat according

to the Curie law. However, when more closely examined at $\chi_M T$ above 200 K, the values were found to gradually increase, as observed in other biradical species having singlet ground state.^{15a,16} The singlet-triplet model using the Bleaney-Bowers equation¹⁷ gave an estimated ΔE_{S-T} value of 2000 K (4.0 kcal mol⁻¹). From these results of absorption, ESR and SQUID measurements, together with the DFT calculations, it can be concluded that dications are singlet ground state with closed-shell nature for **MeS-nTP-C_m²⁺** ($n = 6, 7$) and open-shell nature (i.e., singlet biradical) for **MeS-nTP-C_m²⁺** ($n = 8, 9$). The observed ESR signals would be due to a radical impurity rather than a triplet state of the biradical because the ΔE_{S-T} value is unexpectedly high.¹⁸

In summary, we have succeeded in preparation of stable dication salts of sterically unhindered linear oligomers composed of five-membered heteroaromatics, i.e., **MeS-nTP-C_m²⁺**(SbCl₆⁻)₂. The stable salts enabled us for the first time to study the solid-state properties of this type of linear oligomer dication. The UV-vis-NIR and SQUID measurements together with the results of DFT calculations revealed that a singlet biradical character dominates **MeS-nTP-C_m²⁺** ($n > 8$) without the intermolecular bonding as observed in radical cation π -dimers. Although the calculated results in the relationship among the energies of closed-shell singlet (R), open-shell singlet (U), and triplet (T) are slightly different from the experimental results,¹⁸ the DFT calculations at the B3LYP/6-31G(d) level gave reasonable predictions. In this context, a singlet biradical character in oligothiophene dications may also appear in a shorter oligomer length than the dodecamer, as suggested in the theoretical calculations²⁻⁴ and our previous observations.^{8a}

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Supporting Information Available: Experimental details, Figures S1–S6, Tables S1 and S2, and Cartesian coordinates of the optimized structures of **nTP-C₁²⁺** and **MeS-nTP-C₁²⁺**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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