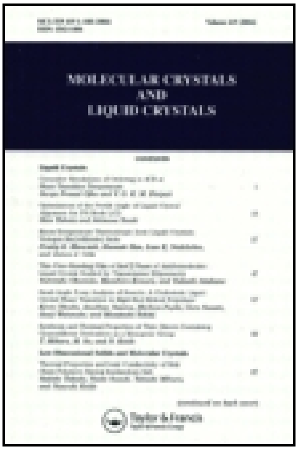

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Moon-Gun Choi [a] , Dong-Jin Jeong [a] & Myongsoo Lee [a]
[a] Department of Chemistry, Yonsei University, 134 Shinchon-Dong, Seoul, 120-749, KOREA

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LIQUID-CRYSTALLINE PROPERTIES OF 5,5'-DIALKYL-2,2':5',2"-TERTHIOPHENE AND ITS π-COMPLEXATION WITH Cp*Ru

MOON-GUN CHOI*, DONG-JIN JEONG and MYONGSOO LEE

Department of Chemistry, Yonsei University, 134 Shinchon-Dong,
Seoul 120-749, KOREA

Abstract A series of dialkylterthiophenes, $CH_3(CH_2)_n$-TTh-$(CH_2)_nCH_3$ (TTh = terthiophene, n=3,5,7,9,11) were synthesized and characterized. All the dialkyl-substituted terthiophenes display smectic mesophase except dibutylterthiophene exhibiting only a crystal melting. The thermal stability of the mesophase of dialkylterthiophene increases with increasing the length of alkyl chains. The complexation of the dialkyl terthiophenes with Cp*Ru suppresses liquid crystallity and all the complexes becomes amorphous.

INTRODUCTION

Substituted oligothiophenes linked at the α-position of the thiophene ring have recently received attention because of their utilities of building blocks for electronic and optical devices.[1] The heterocyclic conjugation of thiophene provides the electrical, nonlinear optical, and electrooptical properties.[2] Recently the chemistry of thiophene transition metal complexes has been of extensively studied to understand the mechanism of industrially important hydrodesulfurization catalytic process.[3] From these efforts, a large number of thiophene transition metal complexes has been prepared and the new chemistry including several bonding modes has been developed.

In the present paper, we have prepared a series of dialkyl substituted terthiophenes with dual purposes. The first is to use thiophene rings as a mesogenic functionality and the other is to use them the transition metal coordination sites. We report the effect of chain length of dialkyl-substituted thiophene to the thermal stability of the mesophase and the mesophase change by the π complexation of Cp*Ru (Cp*=C_5Me_5) at the thiophene ring.

EXPERIMENTAL

All reactions were carried out under an atmosphere of Ar at room temperature using standard Schlenk techniques. The ^{1}H-NMR spectra were obtained from $CDCl_3$ solution on a Bruker DPX 250 spectrometer. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. A Nikon Optiphot 2-pol optical polarized microscope (magnification: x100) equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Elemental analysis was performed with a Perkin Elmer 240 elemental analyzer at Korea Research Institute of Chemical Technology. The $[Cp^*Ru(CH_3CN)_3](OTf)$ was prepared by the reported method.[4]

Synthesis of 5,5"-dialkyl-2,2':5',2"-terthiophene

A series of dialkylterthiophenes, $CH_3(CH_2)_n$-TTh-$(CH_2)_nCH_3$ (TTh =terthiophene, n=3,5,7,9,11) were synthesized with 30-50 % yields according to similar procedures that are described below for 5,5"-dihexyl-2,2':5',2"-terthiophene. A solution of 2-(5-hexyl-thienyl)magnesium bromide prepared from 2-bromo-5-hexylthiophene(0.5g, 2 mmol) with Mg (0.1 g, 4 mmol) in Et_2O (15 mL) was added slowly to a mixture of 2,5-dibromothiophene (0.22g, 0.91 mmol) and $Ni(dppp)Cl_2$ (60 mg, 0.11 mmol) in Et_2O (15 mL). The reaction mixture was heated to reflux for 3 h and poured into water. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was recrystallized from hexane to give yellow crystals(0.11g, 30% yield). ^{1}H NMR($CDCl_3$, δ, ppm) 6.99(s, 2H, J=3.9Hz), 6.70(d, 2H, J=3.5 Hz), 2.81(t, 4H , Tth-C*H*$_2$, J=7.4 Hz), 1.70(m, 4H, Tth-CH_2C*H*$_2$), 1.36(m, 12H, -(C*H*$_2$)$_3$-), 0.91(t, 6H, -C*H*$_3$, J=6.7 Hz). EIMS(70 eV) m/e 416(M^+). Anal. Calcd for $C_{24}H_{32}S_3$: C, 69.18; H, 7.74; S, 23.08. Found: C, 68.75; H, 7.58; S, 22.53. Other analogues also give the satisfactory elemental analyses, ^{1}H NMR spectra and mass spectrometric results.

Reaction of 5,5"-dihexyl-2,2':5',2"-terthiophene with $[Cp^*Ru(CH_3CN)_3](OTf)$

A 100 mL Schlenk flask was charged with $[Cp^*Ru(CH_3CN)_3](OTf)$ (100 mg, 0.197 mmol) and dihexylterthiophene(106 mg, 0.255 mmol) and then purged with Ar two times. CH_2Cl_2 was added and the solution stirred at room temperature. After 14 h, the solution was filtered through celite disk and the solvent was evaporated under vacuum. The residue was washed twice with hexane(10 mL x 2) to give brown sticky solid (65 % yield). ^{1}H NMR($CDCl_3$, δ, ppm) 7.18(d, 1H, Tth-$H_{3'}$, J=3.8 Hz), 7.05(d, 1H, Tth-$H_{3''}$, J=3.6 Hz), 7.01(d, 1H, Tth-$H_{4'}$, J=3.8 Hz), 6.74(d, 1H, Tth-$H_{4''}$, J=3.6 Hz), 6.41(d, 1H, Tth-$H_{3'}$, J=3.2 Hz), 6.26(d, 1H, Tth-H_4, J=3.2 Hz), 1.90(s, 15H, $C_5(CH_3)_5$).

RESULTS AND DISCUSSION

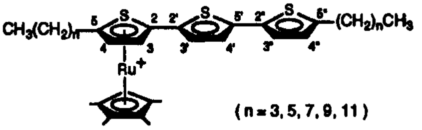
The terthiophene derivatives were synthesized and characterized by 1H NMR, mass spectrometry and elemental analysis. The phase behavior of the mesogenic terthiophene ligands was investigated by a combination techniques of DSC and thermal optical polarized microscopy and is summarized in Table 1. All the dialkylterthiophenes display smectic mesophase except dibutylterthiophene exhibiting only a crystal melting. A representative texture of the smectic A phase of (n-Hexyl)$_2$Tth is shown in Figure 1. The isotropization transition temperature (Ti) of Tth increases with increasing the length of alkyl chains. The ^{1}H NMR spectrum of [Cp*Ru(η^5-(n-Hexyl)$_2$Tth](OTf) shows six magnetically inequivalent protons of the Tth (experimental section). This indicates that Cp*Ru must bind to the outer thiophene to produce six different chemical shifts. Scheme **1** represents the structure and numbering system used for the ruthenium Tth complexes. Two chemical shifts at 6.41 and 6.26 ppm are about 0.5 ppm upfield shifted with respect to uncoordinated Tth. It is well-known that the ^{1}H NMR chemical shift of metal coordinated thiophene are upfield shift of the corresponding free thiophene.[5] The complexation of the mesogenic terthiophene ligands with Cp*Ru suppresses liquid crystallinity and all the complexes becomes amorphous.

TABLE 1 Phase Characterization of the Dialkylterthiophenes (Tth)

Compound	Phase Transitions Temperature (°C)	
	Heating	Cooling
(n-Butyl)$_2$ Tth	k 42 s_A 71 i	i 66 k
(n-Hexyl)$_2$ Tth	k 41 s_A 82 i	i 76 s_A 28 k
(n-Octyl)$_2$ Tth	k 62 s_1 70 s_2 85 s_A 89i	i 87 s_A 83 s_1 67 s_2 52 k
(n-Decyl)$_2$ Tth	k 69 s_A 92 i	i 88 s_A 61 k
(n-Dodecyl)$_2$Tth	k 74 s_A 94 i	i 89 s_A 67 k

s_A=smectic A phase, $s_{1,2}$=unidentified smectic phases, i=isotropic phase.

SCHEME 1



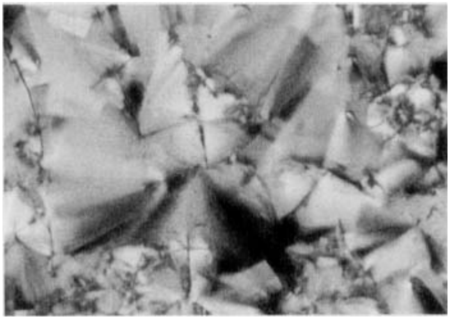


FIGURE 1 Optical polarized micrograph exhibited by smectic A phase of (n-Hexyl)$_2$Tth. (See Color Plate VI).

CONCLUSION

All the dialkyl-substituted terthiophenes display smectic mesophase except dibutylterthiophene exhibiting only a crystal melting. The thermal stability of the mesophase of dialkylterthiophene increases with increasing the length of alkyl chains. The Cp*Ru complexation of terthiophenes show the amorphous phase.

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