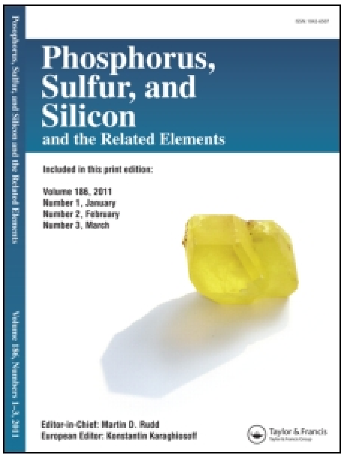

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FURTHER INVESTIGATIONS ON THE SYNTHESIS AND CHARACTERIZATION OF VINYLOGUES OF BIS (ETHYLENEDITHIO) TETRATHIAFULVALENE

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FURTHER INVESTIGATIONS ON THE SYNTHESIS AND CHARACTERIZATION OF VINYLOGUES OF BIS (ETHYLENEDITHIO) TETRATHIAFULVALENE

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A strong electron π-donor, vinylogue bis (ethylenedithio) tetrathiafulvalene (**4**) has been obtained in a six-step from 4,5-bis(benzoylthio)1,3-dithiole-2-thione (**7**) (ca. 40% overall yield), its structure was fully characterized by ^{1}HNMR, FT-IR, MS(EI) and elemental analysis. The yield for the starting material $TEA_2[Zn(DMIT)_2]_2$ is enhanced to 95% by an improved synthetic procedure described herein. Synthesis of aldehyde **14** was investigated in different solvent systems. Compound **10** and the new Horner-Wittig phosphonate (**13**) were first purified as a solid.

Keywords: synthesis; vinylogues BEDT-TTF; synthetic metals; organic solids; organic π-donors; organic conductors

INTRODUCTION

In 1973, Ferraris et al[1] first reported the metallic conductive behavior of a tetracyanoquinodimethane (TCNQ) complex with tetrathiafulvalene (TTF, **1**). Since then, design and synthesis of new electron π-donors and acceptors have received tremendous attention with the view of the development of organic conductors.[2] Among the various organic donors hitherto known, bis(ethylenedithio) tetrathiafulvane (BEDT-TTF,**2**) has produced the most organic superconductors.[3] Structural modifications of the TTF system by insertion of a conjugated spacer group between the two 1,3-dithiol rings represent another

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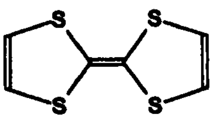
interesting class of donor molecules. The advantages of donor systems with extended π-conjugation are as follows: 1, the oxidized states responsible for conduction in the charge-transfer salts should be significantly stabilized as a result of increased delocalization of the positive charge(s) (i.e., decreased coulombic repulsion) offering the possibility of noncorrelated mechanisms of Conductivity, if the dication states are sufficiently stable.[4] 2, extended donors are highly polarizable species by virtue of a large number of chalcogen atoms and π-bonds, which should favor strong intermolecular interactions (i.e., increased dimensionality).[2c,5] 3, geometrically more flexible structures can be obtained, offering the possibility of novel packing motifs. 4, there is scope for obtaining molecular conductors or magnets based upon entirely new π-frame works rather than TTF and its very close analogues.[6]

Extensive studies have been directed towards vinylogues of TTF. Yoshida and coworkers[7] reported the synthesis of the parent system **3** in 1983, and very recently, the BEDT-TTF vinylogue **4** was prepared concurrently by three groups.[8–10]



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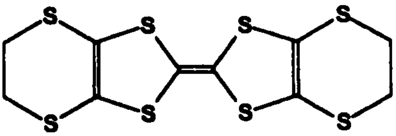

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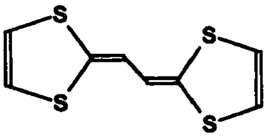

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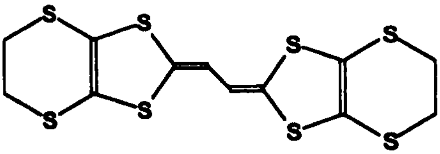


4

All donors of **1–4** show two reversible oxidation waves (SCE) at: **1**, 0.35 and 0.77V; **2**, 0.49 and 0.74V; **3**, 0.20 and 0.36V; **4**, 0.46 and 0.66V respectively. This clearly indicates that vinylogues **3** and **4** are stronger electron donors than TTF(**1**) and BEDT-TTF (**2**), and also the E_2-E_1 values of **3** and **4** is smaller than that of **1** and **2**, indicative of decreased Coulombic repulsions in the dications derived from them.

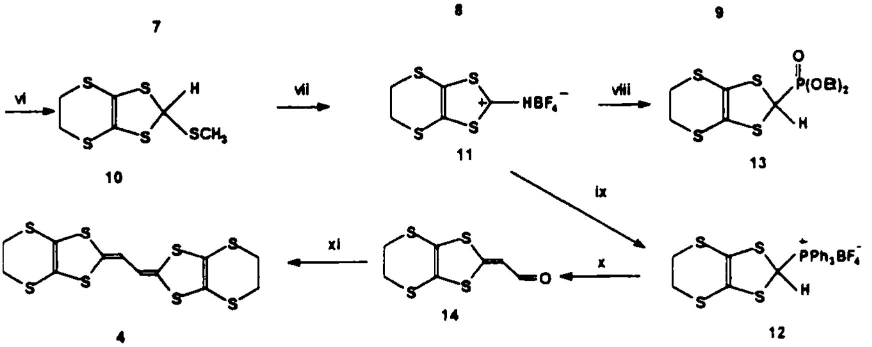
In the present work, we now report analogous methodology for the efficient preparation of vinylogue BEDT-TTF(4) according to the methods described in ref.[10–15]. However, the preparation and characterization of some key intermediates and product **4** have been further improved.

EXPERIMENTAL SECTION

Melting points were recorded on a X-4 type microscope apparatus and are uncorrected. ^1H NMR spectra were obtained with a Varian XL-200 (200MHz) instrument using tetramethyl silane as internal standard, chemical shifts are given in ppm. Mass spectra were measured using a Finnigan-4201C Mass spectrometer, with an electron-impact source at 70ev. Elemental analyses were performed by the Analysis & Measurement Center of our Institute with a Carlo Erba 1106 apparatus. Infrared spectra were recorded on a Bruker IFS-113V Fourier Transform Infrared spectro-photometer in the region of 4000–400 cm^{-1} with KBr pellets at room temperature. Reagents and solvents were purified before use.

The synthetic scheme is shown in scheme 1:

Regents and conditions: i, DMF, refluxing for 6hrs; ii, $ZnCl_2/MeOH-H_2O$, r.t. 5min, then Et_4NBr/H_2O, r.t. 3hrs; iii, PhCOCl/Acetone, r.t. 2hrs; iv, NaOEt/EtOH, $BrCH_2CH_2Br$, 2hrs; v, $(CH_3O)_2SO_2$, 70°C, 30min; HOAc, 0°C 5min.;



SCHEME 1

HBF_4-Et_2O, °C 10min; vi, $NaBH_4$/EtOH, 0°C, 1hr, then r.t., 0.5hr; vii, Ac_2O, 0°C, HBF_4-Et_2O, 0°C 0.5hr; viii, NaI/$P(OEt)_3$/CH_3CN, r.t. 1hr; ix, PPh_3/ CH_3CN, r.t. 1hr; x, Et_3N, glyoxal (aqu.)/THF or CH_3CN, 3hrs; xi, compound **13**/THF, −78°C, BuLi, 15min., then aldehyde **14**, −78°C, 0.5hr, then r.t. 3hrs.

Bis(tetraethylammonium) bis (1,3-dithiol-2-thione-4,5-dithiolato zincate (6)[16]

Finely divided sodium (23.0g, 1mol) was introduced into a three-necked 1L flask equipped with a magnetic stirrer, a dropping funnel and an N_2 inlet. Carbon disulfide (200mL, 3.3 mol) was added in one portion, and the flask was placed in an oil bath, 5mL DMF was added at first, and the mixture was heated to 40°C to initiate the exothermic reaction. After the reduction reaction occurred, the oil bath was removed, and 195mL DMF was added dropwise, so that the reaction mixture maintained refluxing smoothly. After addition of DMF, the mixture were heated to reflux for 6hr, then cooled to room temperature, the residual sodium was carefully destroyed by adding methanol dropwise. After complete destruction of the sodium, a mixture of water (400mL) and methanol (400mL) was added in one portion. Anhydrous $ZnCl_2$ (20g, 0.15mol) was dissolved in Conc. $NH_3.H_2O$(400mL) and added in one portion. The mixture was stirred for 10min after which Et_4NBr (55g, 0.25mol) dissolved in 250mL H_2O was added in one portion and stirring was continued for 3hr. The red crystalline precipitate was filtered off, washed thoroughly with 1000mL water (by suspending the precipitate in 1000mL water and stirring for 10min. followed by filtration). The red solid was washed with methanol (200mL), and dried under reduced pressure affording **6** as red crystals 88g, (95%). m.p. 212–214°C (lit[16] 206–208 °C).

Compound **7** and **8** were prepared in 84% and 90% yields respectively according to the procedure described in lit.[16]

2-methylithio-5,6-dihydro-1,3-dithiolo[4,5-b][1,4]dithiin-2-ium tetrafluoro-borate (9)

6.6g (30mmol) of 2-thione (**8**) was suspended in 30mL freshly distilled dimethyl sulphate, and the mixture was heated to ~70°C under nitrogen atmosphere. After 30min dissolution was achieved. The reaction mixture was cooled to 0°C and 3 mL glacial acetic acid was added dropwise, followed by dropwise addition of 4.5 mL (32mmol) tetrafluoroboric acid-diethyl ether complex. Stirring was continued for 30min at 0°C and 300mL anhydrous diethyl ether was added. The orange precipitate was filtered off, washed thoroughly with anhydrous diethyl ether (200mL), collected and recrystallized from methanol-diethyl ether to afford salt **9** as a yellow solid; 9.0g (yield 95%), m.p. 122–124°C (lit.[11] 124–126°C). ^{1}H NMR (DMSO-d_6), δ 3.35 (s,3H, SCH_3), 3.44 (s, 4H,SCH_2), IR(KBr), (ν,cm^{-1}) 2930, 2870 (CH_2), 1480 (C═C). $C_6H_7BF_4S_5$ Calc., C: 22.08; H: 2.16; S: 49.14. Found, C: 21.79; H: 2.13; S: 49.10.

2-methylthio-5,6-dihydro-1,3-dithiolo[4,5-b][1,4] dithiin (10)

To a stirred suspension of salt **9** (8.2g, 25mmol) in 140mL absolute ethanol, 1.0g (28mmol) $NaBH_4$ was added at such speed that the reaction temperature was maintained under 0°C (by cooling with ice-salt bath). After the addition, the reaction mixture was stirred at r.t. for a further 1.5hr under nitrogen. The solvent was removed under reduced pressure, and the residue was dissolved in 200mL chloroform, washed with water (50mL × 2), dried with anhydrous $MgSO_4$ and concentrated in vacuum to afford the crude product **10** as a light brown oil, which solidified after cooling in a refrigerator, recrystallization from chloroform/petroleum ether (60–90°C) (1 : 1) gave **10** as white plates 5.9g (98% yield). m.p. 45–46°C. ^{1}H NMR($CDCl_3$), δ 2.25 (s, 3H, SCH_3), 3.16–3.44 (m, 4H, SCH_2), 5.78 (s, 1H,CH). IR(KBr), (ν,cm^{-1}) 2905 (CH_2), 1410 (C═C), 730 (C-S). MS (EI), m/z = 240 (M^+, 18.8%), 193 (M^+ − SCH_3, 100%). $C_6H_8S_5$ Calc., C: 29.97; H: 3.35; S: 66.68. Found, C: 29.78; H: 3.23; S: 66.72.

5,6-dihydro-1,3-dithiolo [4,5-b] dithiin-2-ium tetrafluoroborate (11)

To compound **10** (6g, 25mmol) suspended in 60mL acetic anhydride and cooled to 0°C by an ice-salt bath under nitrogen was added diethyl ether-tetrafluoroboric acid (3.7mL, 26mmol) dropwise through a dropping funnel. The temperature was maintained under 0°C and the color of the solution intensified. After stirring for a further 30min at 0°C, 200mL dry diethyl ether was added to precipitate the products which were filtered off and washed thoroughly with dry diethyl ether. After drying 6.5g (92% yield) of **11** was obtained. Purification of **11** by crystallisation from ethanol-cyclohexane gives analytically pure samples of salt **11** as a yellow solid. m.p. 130°C (dec.) (lit.[11] 110°C,dec). ^{1}H NMR(DMSO-d_6), δ3.20–3.40 (m,4H, SCH_2), 6.65 (s,1H,CH). IR (KBr), (ν,cm^{-1}) 3020, 2980 (CH_2), 1400 (C═C), 725(C-S). $C_5H_5BF_4S_4$, calc., C: 21.43; H: 1.80; S: 45.78. found, C: 21.45; H: 1.77; S: 44.97.

2-triphenylphosphonio-5,6-dihydro-1,3-dithiolo[4,5-b][1,4] dithiin tetrafluoro-borate (12)

A solution of 5.6g (20mmol) salt **11** dissolved in 140ml dry acetonitrile was degassed by bubbling nitrogen. 5.2g (20mmol) of triphenyl phosphine was added in one portion at r.t., during which time the white precipitate appeared. Stirring was continued for 1 hr more and the solvent was removed in vacuo. The resulting solid was washed with anhydrous diethyl ether (200mL), recrystallized from ethanol-hexane to afford salt **12** as a white solid 10.5g (97%). m.p. 185–187°C (lit.[11] 183–185°C). ^1H NMR (DMSO-d_6), δ 2.80–3.15 (m,4H,SCH_2), 7.50–8.00 (m,15H, aromatic-H), 8.19 (s, 1H, CH). IR(KBr), (ν,cm^{-1}): 2930 (CH_2), 1440 (Ph), 1050 (P-O-C). $C_{23}H_{20}BF_4PS_4$ calc., C: 50.92; H: 3.72; S: 23.65. found, C: 50.87; H: 3.41; S: 23.02.

2-diethoxyphosphoryl-5,6-dihydro-1,3-dithiolo[4,5-b] [1,4] dithiin (13)

3.36g (12mmol) of salt **11** and 1.95g sodium iodide (13mmol) were dissolved in 75ml dry acetonitrile and stirred under nitrogen. 2mL (15mmol) of freshly distilled triethyl phosphite was added at r.t. and stirring was continued for a further 30min. The solvent was evaporated under vacuum, and the residue dissolved in 150mL chloroform, washed with water (60mL × 2), dried with anhydrous $MgSO_4$. Evaporation of the chloroform afforded crude compound **13** as a slightly brown oil. Further purification could be achieved by chromatography of the oil on silica gel eluting with chloroform/petroleum ether (60–90°C) (1:2, v/v). After work up, compound **13** was obtained as a white solid, 3.6g (91%), m.p. 59–60°C. ^1H NMR($CDCl_3$), δ 1.38 (t,3H,J = 6.2Hz,CH_3), 3.24 (m,4H,SCH_2), 4.28 (m,4H,CH_2), 4.78 (d, 1H,J = 6.2Hz,CH). IR(KBr), (ν,cm^{-1}), 2970 (CH_2), 1050 (P-O-C), 1230(P=O). MS (EI), m/z = 330 (M^+,17.3%), 193(M^+-$PO(OEt)_2$, 100%), $C_9H_{15}O_3PS_4$, calc., C: 32.71; H: 4.58; S: 38.81, found, C: 32.60; H: 4.53; S: 38.92.

4,5-(ethylenedithio)-2-(formylmethylene)1,3-dithiole (14).

Method A: 1.62g (3mmol) of salt **12** was dissolved in 30 mL dry THF, and 0.5mL (3.6mmol) dry triethylamine and 1.0mL (8mmol) glyoxal (40% aqueous solution) were added successively under nitrogen. The reaction mixture was stirred for 3hr at r.t.. The solvent was evaporated in vacuo at T ≤ 40°C, and the residue was dissolved in 100mL chloroform and washed with water (50mL × 2), dried with anhydrous $MgSO_4$ and filtered quickly through a short column of silica eluting with dichloromethane-hexane (1:2, v/v) followed by neat dichloromethane to afford compound **14** as yellow-needles, 0.55g (78%), m.p. 120–122°C (lit.[11] 125–126°C). ^{1}H NMR ($CDCl_3$), δ 3.38 (s,4H,SCH_2), 6.65 (d, J = 2.7Hz, 1H, CH), 9.39(d, J = 2.7Hz, 1H, CHO). IR (KBr), (ν,cm^{-1}): 2924 (CH_2) 1619, 1602 (CHO), 1445 (C═C). MS(EI), m/z = 234 (M^+,100%), 206 (M^+-CHO, 30%). $C_7H_6OS_4$, calc., C: 35.87; H: 2.58; S:54.72, found, C: 35.60; H: 2.44; S: 54.40.

Method B: 1.62g (3mmol) of salt **12** was dissolved in 30mL acetonitrile, and 0.50mL (3.6mmol) triethylamine and 1.0mL (8mmol) glyoxal (40% aqueous solution) were added under nitrogen, stirring was continued for a further 3hr at r.t.. Standard work up led to the isolation of aldehyde **14** (0.45g, 65%), identical with the sample prepared by method A.

Method C: Similar to method A, except that the solvent is replaced by a mixture of dry THF and dry acetionitrile (30mL, 1 : 1,v/v). After work up 0.5g of aldehyde **14** was obtained (71% yield).

BEDT-TTF vinylogue 4

0.495g(1.5mmol) of phosphonate **13** was dissolved in 15mL dry THF in a 100mL three-necked flask equipped with a nitrogen balloon, magnetic stirrer, rubber septum and a dropping funnel. The solution was cooled to −78°C by a liquid nitrogen-isoamylacetate bath. A solution of 1.8mL (1.62mmol) butyllithium (0.9M solution in n-heptane) was syringed in dropwise, and the mixture stirred for 15min at −78°C. A solution of aldehyde **14** (0.351g, 1.5 mmol) in dry THF (10mL) was added dropwise through the dropping funnel. After addition, the mixture was maintained for 30min at −78°C, followed by slow warming to r.t. and stirring for a further 4hr. The red-brown solid was collected by filtration, washed thoroughly with dry THF, followed by anhydrous ethanol, and then recrystallized from DMSO (100mL, 120°C) to give **4** as yellow-greenish plates 0.50g (81%), m.p. 275°C(dec) (lit.[10] 245°C,dec.). ^{1}H NMR (CS_2-$CDCl_3$), δ 3.27(s, 8H, SCH_2),5.74 (s,2H, CH). FT- IR (KBr), (ν,cm^{-1}), 2920(CH_2), 1499, 1407 (C═C), 810 (C-S). MS (EI) m/z = 410 (M+, 100%), 382 (M+-$(CH_2)_2$, 88.7%), $C_{12}H_{10}S_8$, calc., C: 35.09; H: 2.45; S: 62.45, found C: 35.09; H: 2.41; S: 61.51.

DISCUSSION

It should be appreciated that the synthesis of more highly-substituted and conjugated donor molecules (compare with TTF and BEDT-TTF) can be time-consuming and experimentally very demanding. We have developed several important modifications that significantly improve the yield of several key intermediates. Our key starting material was the known zinc chelate $TEA_2[Zn(DMIT)]_2$ (**6**), we have prepared **6** by a much improved synthetic procedure. The DMF-mediated reduction of carbon disulfide by alkali metals in the most convenient way, but since the use of potassium in this reaction can lead to explosions, the use of sodium was considered from the viewpoint of safety. The synthetic approach which was mainly developed in the laboratories of Hoyer[17], relies on the utilization of the cheap starting materials (CS_2 + Na), and the synthesis can be performed on a one-mole scale without problems. We found that the reduction reaction could occur smoothly under the refluxing condition, and the yield of **6** can be improved to 95% (compared with lit.[16], 86%). In our modification, only a small amount of DMF should be added at the beginning of the reaction, and after the exthomic reduction reaction was initiated, the remaining DMF can be added slowly to maintain a vigorous refluxing (60°C oil bath).

The known thione **8**, which was prepared according to the method described in ref.[16], was methylated using neat dimethyl sulphate to yield **9** as its tetrafluoroborate salt (>90% yield), which can be directly used in the next step without any purification. However the reaction temperature should be maintained at ~70°C and no higher than 90°C, and the reaction time should be no longer than 1hr, lest the color of the products be deeply darkened with the appearance of a brown oil, which leads to difficulties for the next step reaction. Compound **10** was obtained as white plates (m.p. 45–46°C, >95% yield) by reduction of tetrafluoroborate salt **9** with a slight excess of sodium borohydride in absolute ethanol. Bryce et al[11] reported **10** as an oil. Purification of **10** can be conducted by recrystallization from chloroform-petroleum ether (1:2, v/v) rather than column chromatography, a time-consuming procedure, to afford an analytically pure product. Crude product **10** can be converted to salt **11** (yield 90%) readily upon treatment with acetic anhydride followed by dropwise addition of tetrafluoroboric acid-diethyl ether complex. Analytically pure **11** can be obtained by recrystalization of the crude salt from ethanol-cyclohexane, however, this process can often be omitted from the pointview of the synthetic reactions, because of the instability of the salt **11**. Salt **11** yields phosphonate ester **13** (>90% yield) by treatment with triethyl phosphite in the presence of sodium iodide. Compound **13** can be further purified by column chromatography through a silica gel eluting with chloroform/petroleum ether (60–90°C) (1:2, v/v), and was obtained as a white solid (m.p. 58–60°C), rather than slightly colored oil[11]. It should be noted that compound **13** becomes brown slowly on exposure to air or daylight, but can be stored under nitrogen at −4°C for about two weeks without obvious decomposition. It is suggested that compound **13** be used as soon as possible after its preparation. The corresponding salt **12** was obtained by treatment of salt **11** with equal molar of triphenyl phosphine in dry acetonitrile (>95%). Salt **12** is stable at ambient for at least one month.

Aldehyde **14** was prepared in different solvent systems, i.e., THF, THF-CH_3CN and CH_3CN. We find that the solvent can affect both the yield of **14** and its ease of the purification. In neat THF, the product can be easily isolated and purified (yield ~78%), however, in neat CH_3CN the yield of **14** decreased to 65% and some difficulties appeared during the purification of **14** by column chromatography. Hansen et al[10] reported that aldehyde **14** can also be obtained from 2-triphenylphosphino-5,6-dihydro-1,3-dithiol [4,5-b][1,4] dithiin triflate salts and glyoxal in the presence of triethylamine in acetonitrile in yield as high as 98%. For the preparation of **14** from salt **12**, the yield is not as high. When the mixture of THF and CH_3CN was used as the solvent in the preparation of aldehyde **14**, the yield is decreased slightly compared with that of neat THF as solvent (71% via 78%), but the purification of **14** is easier than that in method B.

The synthesis of vinylogue bis(ethylenedithio)(**4**) was achieved by reacting the Horner-Wittig phosphonate **13** with a slight excess of n-butyllithium at −78°C followed by condensation with aldehyde **14**. Purification could be effected by recrystallization from DMSO (100mg/20mL). Hansen et al[10] reported that **4** was not volatile enough to determine the EI mass spectrum. We were able to obtain the EI mass spectrum of **4** successfully with electron impact source at 70ev.(m/z = 410,M^+, 100%; 382,M^+-$(CH_2)_2$, 88.7%; 354,M^+-$(CH_2)_4$, 5.27%; 205,$M^+/2$, 10.2%). Compound **4** is almost insoluble in common organic solvent such as $CHCl_3$, CH_2Cl_2, THF, cool DMSO, EtOH, CH_3CN, etc. Although it is difficult to obtain the ^1H NMR spectrum of **4** from DMSO-d_6 solution due to its limited solubility, a mixture of CS_2 and $CDCl_3$ affords sufficient solubility to obtain the ^1H NMR spectrum. The ultra-violet absorption spectrum of **4** in solvents are as follows: $\lambda max(CS_2)$ 412nm ($\log_\epsilon$, 4.60); $\lambda max(THF)$ 396nm ($\log_\epsilon$, 4.38), 418nm ($\log_\epsilon$, 4.58); $\lambda max(EtOH)$ 390nm ($\log_\epsilon$, 4.12), which is similar to that reported by Hansen et al[10]

Single crystals of a 1:1 charge transfer complex formed between electron donor **4** and acceptor TCNQ shows room temperature conductivity at $\sigma_0 = 33$ Scm^{-1}. The crystal structure of CT complex will be obtained soon. Spectral properties (UV-Vis, FT-IR, XPS, Raman Scating) and crystal structure of TCNQ complex of **4** will be published elsewhere.

Investigation on the preparation and conductive properties of other charge transfer complex and radical cation salts based on the donor **4** are being undertaken in our group.

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