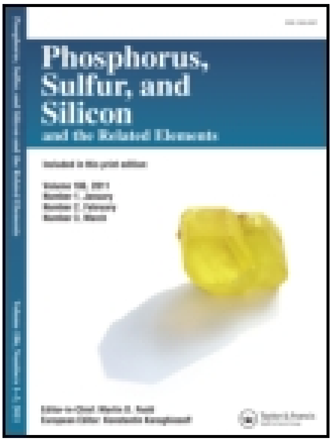

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis and Characterization of Nitrobenzoylthiourea Derivatives as Potential Conductive Biodegradable Thin Films

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To cite this article: Wan M. Khairul, Khalisah Asilah Mokhtar, M. I. N. Isa, A. S. Samsudin, Hasyiya Karimah Adli, Saidatul Radhiah Ghazali & Adibah Izzati Daud (2014) Synthesis and Characterization of Nitrobenzoylthiourea Derivatives as Potential Conductive Biodegradable Thin Films, Phosphorus, Sulfur, and Silicon and the Related Elements, 189:5, 640-651, DOI: 10.1080/10426507.2013.844137

To link to this article: http://dx.doi.org/10.1080/10426507.2013.844137

Phosphorus, Sulfur, and Silicon, 189:640–651, 2014

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2013.844137

SYNTHESIS AND CHARACTERIZATION OF NITROBENZOYLTHIOUREA DERIVATIVES AS POTENTIAL CONDUCTIVE BIODEGRADABLE THIN FILMS

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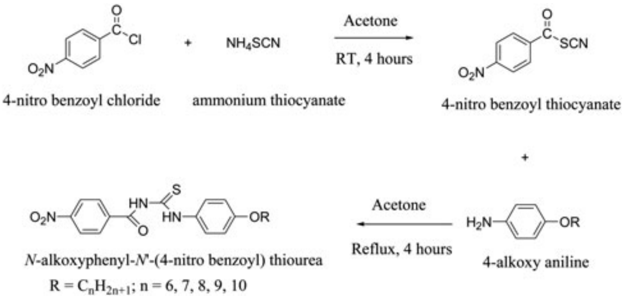
GRAPHICAL ABSTRACT



Abstract *The application of thiourea derivatives as conjugated molecular wire candidates in the field of material sciences has attracted great attention recently. To date, conjugated thiourea systems as molecular wires are surprisingly unexplored although the well-known rigid* π*-systems promise a wide range of electronic properties. Due to this matter, five novel thiourea derivatives A-ArC(O)NHC(S)NHAr-D with polar head and tail groups, namely* NO_2 *(acceptor A) and alkoxy with varying chain lengths (donor* D = OC_nH_{2n+1}*,* $n = 6, 7, 8, 9, 10$*), were successfully synthesized and characterized. All compounds were characterized by IR, UV-vis,* ^1H *and* ^{13}C *NMR spectroscopy, and CHNS elemental microanalysis. The investigation of their potential as dopant systems in polymer conducting films has been accomplished by incorporating of chitosan via the solution casting technique.*

Received 25 April 2013; accepted 10 September 2013.

The authors would like to thank Department of Chemical Sciences, Institute of Marine Biotechnology (IMB), and Department of Physical Sciences, Faculty of Science and Technology, Universiti Malaysia Terengganu for the technical and research support.

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The conductivity values were obtained using impedance spectroscopy. They show that the ionic conductivities of the N-(4-alkoxyphenyl)-N'-(4-nitrobenzoyl)thioureas increase with increasing chain length of the alkoxy chain. The compounds exhibit great potential for the exploration of future applications as doping systems in conductive materials.

Keywords Thiourea; molecular wire; conductive thin film

INTRODUCTION

In recent years, a widespread interest in convenient use of smaller, lighter, quicker, and more efficient electronic devices is observed. The focus for current research on molecular electronics is due to the process of miniaturization in the field of information processing technology according to the Moore's Law.[1] However, it is challenging to find suitable and applicable molecular materials for their utilization in molecular electronic devices. Recently, organic polymer thin films have attracted a great deal of attention from researchers in the field of molecular electronic devices.[2,3] A large variety of techniques have been developed for thin film deposition such as spray pyrolysis technique,[4,5] chemical vapor deposition (CVD)[6] spin coating,[7] solution casting technique[8] and inkjet printing or stamping.[9] Among different techniques for organic thin film deposition, solution casting technique has been chosen in this study due to its advantages such as applicability of low-temperature processes, requirement of only small sample amounts and uniform film thickness obtained.[10] Moreover, this general and convenient method can be applied to form highly uniform thin films on all kinds of substrates.[11]

It is known that for the past few decades, thiourea derivatives with their resonance structures have been widely studied as versatile ligands in various applications. This is due to their unique properties which enable to coordinate with numerous transition metal ions as monodentate or bidentate ligands.[12] They are classical additives for the electro deposition of copper and other metals,[13] corrosion inhibitors,[14,15] vulcanization accelerators,[16] and pharmaceuticals products.[17] Meanwhile, the thiourea system has turned out to be a great candidate to construct D-A molecular wire compounds, which can act as excellent transporters.[18,19] The electron transportation through these compounds which is widely known to have π-conjugated system has become the fundamental importance as molecular wire.[20] They can act as the simplest electronic component for the conduction of current. These compounds should display ideal characteristics such as wide concentration range, fast response time and good selectivity coefficient for many cations.

To date, to the best of our knowledge, the idea and work on manipulating conjugated thiourea derivatives as molecular wire candidate has never been carried out and reported beyond our research team. Therefore, this present work involves the materials syntheses, characterization, data analysis as well as the development of thin films by solution casting technique. In addition, their behavior and characteristics including their electrical properties via formation of thin film by solution casting techniques were also carried out. As it is processed in a final application, a thin film should be best measured for the material properties including the electrical properties.[21] The so-called molecular wire were synthesized and studied by several chemical analyses such as IR, ^{1}H and ^{13}C NMR, UV-Visible spectroscopy, and CHNS elemental analysis as well as impedance measurements for their conductivity analysis.

RESULTS AND DISCUSSION

Spectroscopic Studies

The ^1H NMR spectra for this series of compounds show methyl resonances in the range of δ_H 0.91–0.93 ppm while protons for alkyl group were observed in the range δ_H 1.32–1.81 ppm. For OCH_2, the signals were detected in the range δ_H 3.97–3.99 ppm as triplets as reported previously for similar systems.[22] The aromatic protons were observed in the range δ_H 6.95–8.41 ppm and show a pseudo-doublet for the AB system of the arene protons which is due to the *para*-substitution of the aromatic rings in these compounds.[23] Furthermore, two singlet resonances due to two NH groups in these compounds were observed at δ_H 9.18–9.36 ppm and δ_H 12.21–12.24 ppm. The ^1H NMR data for all compounds synthesized in this series are shown in Table 1.

The ^{13}C NMR spectra for the series of these derivatives show methyl group resonances at δ_C 14.1 ppm and carbon resonances for alkyl groups in each compounds at δ_C 22.6–31.9 ppm. Chemical shifts for CH_2O in this series were observed at δ_C 68.3 ppm and resonances for both aromatic ring carbons were observed in the range δ_C 114.7–128.8 ppm. One resonance each was observed in the range δ_C 164.9–165.0 ppm and δ_C 177.9–178.1 ppm which corresponds to the C=O and C=S carbons respectively. The C=O and C=S resonances were slightly de-shielded to higher chemical shifts which may be due to intramolecular hydrogen bonding of the compounds and the electronegativity of oxygen and sulfur.[22,23]. Table 2 shows the ^{13}C NMR data for all compounds in this series.

The infrared spectra of these derivatives show six absorption bands of interest namely ν(NH), ν(CH), ν(C=O), ν(N=O), ν(C–O) and ν(C=S). Table 3 shows the absorption data for these derivatives.

For this series of compounds, it can be clearly seen that the absorption bands of NO_2 appear in the range of 1533 to 1515 cm^{-1} and 1350 to 1342 cm^{-1} due to resonance effects. The absorption bands for a nitro group should be shifted to lower frequencies at 1550–1490 cm^{-1} and 1355–1315 cm^{-1} due to conjugation with an aromatic ring.[24] In this series of compounds, the nitro group is located in the *para*-position of the aromatic ring and the vibration frequencies are in the corresponding range. The absorption bands of C=S in these compounds were observed at 713 to 709 cm^{-1}, which confirmed the formation of the thioureas.[25–27] The electronic absorption spectra of **1–5** were recorded in dichloromethane and show two principal bands which were expected to arise from the C=O and C=S moieties. Table 4 shows the principal UV-vis absorption data of **1–5**.

Functional carbonyl (C=O) and thiocarbonyl (C=S) groups exhibit two principal UV transitions, the allowed π–π^* transition (190 nm) and the forbidden n–π^* (280 nm) transition.[25] However, under usual experimental conditions only the forbidden n–π^* transition is commonly observed. Due to the extended π-electron conjugation, the absorption peak is red-shifted (bathochromic shift). Therefore, the absorption bands for C=O and C=S chromophores in thiourea derivatives appear in the range of 232.0 to 233.6 nm and 256.2 to 260.0 nm, respectively, since the carbonyl and thione groups in thiourea derivatives are part of the conjugated system.[28] Furthermore, the electron withdrawing NO_2 group also exhibits a pronounced bathochromic shift of the n–π^* transition and π–π^* transition. It shows a broad band at of 256 to 260 nm, due to the conjugation effect. The broad absorption bands observed in the region between 250 to 350 nm is due to π-conjugation of the compounds with the phenyl ring (π–π^* transition), probably arising from orbital overlapping between C=S and NO_2.

Table 1 ^{1}H NMR data for all synthesized compounds

Compound	Moieties	Chemical shift δ_H (ppm)
1	(t, $J_{HH} = 7$ Hz, 3H, CH_3)	0.93
	(m, 6H, 3 × CH_2)	1.35–1.50
	(m, 2H, CH_2)	1.81
	(t, $J_{HH} = 6$ Hz, 2H, CH_2)	3.99
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4) (pseudo-d, $J_{HH} = 9$ Hz,	6.96
	2H, C_6H_4)	7.54
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.11
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.39
	(2 × s, 1H, NH)	9.29, 12.23
2	(t, $J_{HH} = 7$ Hz, 3H, CH_3)	0.92
	(m, 8H, 4 × CH_2)	1.36–1.48
	(m, 2H, CH_2)	1.76
	(t, $J_{HH} = 6$ Hz, 2H, CH_2)	3.97
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4) (pseudo-d, $J_{HH} = 9$ Hz,	6.97
	2H, C_6H_4)	7.55
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.11
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.39
	(2 × s, 1H, NH)	9.25, 12.22
3	(t, $J_{HH} = 7$ Hz, 3H, CH_3)	0.92
	(m, 10H, 5 × CH_2)	1.32–1.37
	(m, 2H, CH_2)	1.73
	(t, $J_{HH} = 6$ Hz, 2H, CH_2)	3.99
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4) (pseudo-d, $J_{HH} = 9$ Hz,	6.96
	2H, C_6H_4)	7.56
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.11
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.40
	(2 × s, 1H, NH)	9.22, 12.22
4	(t, $J_{HH} = 7$ Hz, 3H, CH_3)	0.91
	(m, 12H, 6 × CH_2)	1.38–1.51
	(m, 2H, CH_2)	1.76
	(t, $J_{HH} = 6$ Hz, 2H, CH_2)	3.97
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4) (pseudo-d, $J_{HH} = 9$ Hz,	6.95
	2H, C_6H_4)	7.55
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.13
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.40
	(2 × s, 1H, NH)	9.36, 12.24
5	(t, $J_{HH} = 7$ Hz, 3H, CH_3)	0.91
	(m, 14H, 7 × CH_2)	1.35–1.50
	(m, 2H, CH_2)	1.79
	(t, $J_{HH} = 6$ Hz, 2H, CH_2)	3.98
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4) (pseudo-d, $J_{HH} = 9$ Hz,	6.95
	2H, C_6H_4)	7.56
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.12
	(pseudo-d, $J_{HH} = 9$ Hz, 2H, C_6H_4)	8.41
	(2 × s, 1H, NH)	9.18, 12.21

CHNS Elemental Analysis

CHNS elemental analysis was used to determine the percentage of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). Elemental analysis can be used to determine the purity of the compounds of interest by comparison between experimental and theoretical percentage of the elements.[29] Table 5 shows CHNS analytical data of the thiourea derivatives.

Table 2 The data of ^{13}C NMR spectra for compounds **1–5**

Compound	Moiety	Chemical Shift, δ_C (ppm)
1	(s, CH_3)	14.1
	(4 × s, 4 × CH_2)	22.6, 25.7, 29.2, 31.6
	(s, CH_2O)	68.3
	(8 × s, C_6H_4)	114.7, 115.0, 122.3, 124.0, 124.3, 125.8, 128.3,
	(s, C=O)	128.9
	(s, C=S)	165.0
		177.9
2	(s, CH_3)	14.1
	(5 × s, 5 × CH_2)	22.6, 26.0, 29.1, 29.2, 31.8
	(s, CH_2O)	68.3
	(8 × s, C_6H_4)	114.7, 122.3, 124.0, 124.3, 125.7, 128.2, 128.9,
	(s, C=O)	129.7
	(s, C=S)	165.0
		177.9
3	(s, CH_3)	14.1
	(6 × s, 6 × CH_2)	22.7, 26.0, 29.2, 29.3, 29.4, 31.8
	(s, CH_2O)	68.3
	(8 × s, C_6H_4)	114.7, 115.0, 122.3, 124.0, 124.3, 125.7, 128.2,
	(s, C=O)	128.9
	(s, C=S)	164.9
		178.0
4	(s, CH_3)	14.1
	(7 × s, 7 × CH_2)	22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 31.9
	(s, CH_2O)	68.3
	(8 × s, C_6H_4)	114.7, 115.0, 122.3, 124.0, 124.3, 125.8, 128.2,
	(s, C=O)	128.9
	(s, C=S)	165.0
		178.1
5	(s, CH_3)	14.1
	(8 × s, 8 × CH_2)	22.7, 26.0, 29.2, 29.3, 29.3, 29.4, 29.6, 31.9
	(s, CH_2-O)	68.3
	(8 × s, C_6H_4)	114.7, 115.0, 122.3, 124.0, 124.4, 125.7, 128.2,
	(s, C=O)	128.8
	(s, C=S)	164.9
		177.9

Table 3 IR Absorption data of the nitrobenzoylthioureas **1**–**5**

Compound	ν(NH) cm^{-1}	ν(CH) cm^{-1}	ν(C=O) cm^{-1}	ν(NO_2) cm^{-1}	ν(C–O) cm^{-1}	ν(C=S) cm^{-1}
1 Intensity	3306 (m)	2857 (m)	1651 (m)	1524 (m) 1348 (m)	1112 (m)	711 (m)
2 Intensity	3238 (m)	2855 (s)	1677 (s)	1515 (m) 1351 (m)	1111 (m)	710 (m)
3 Intensity	3326 (s)	2854 (s)	1675 (m)	1518 (s) 1344 (m)	1110 (m)	713 (m)
4 Intensity	3350 (m)	2853 (s)	1661 (m)	1528 (s) 1342 (m)	1113 (m)	709 (m)
5 Intensity	3341 (s)	2853 (s)	1674 (m)	1533 (m) 1343 (m)	1111 (m)	709 (m)

Table 4 The principal UV-vis absorption data of nitrobenzoylthioureas

Compound	Concentration/M	C=O λ/nm (ε/M^{-1}cm^{-1})	C=S λ/nm (ε/M^{-1}cm^{-1})
1	2.3633×10^{-5}	232.0 (38307)	258.0 (22566)
2	2.2208×10^{-5}	232.0 (39941)	258.0 (23532)
3	2.8310×10^{-5}	233.6 (33324)	257.0 (22501)
4	2.7144×10^{-5}	233.6 (34593)	260.0 (23755)
5	2.9090×10^{-5}	232.2 (33957)	256.2 (22417)

All synthesized thioureas show good results of C, H, N, and S in elemental analysis with only slight deviations from the theoretical percentages.

Electrical Conductivity Study

The impedance spectra (or Cole–Cole plot) at ambient temperature obtained on conductive thin film based on chitosan doped with different thioureas is shown in Figure 1. The conductivity values of the samples were calculated by use of equation (1). From the plots of negative imaginary impedance, Z_i versus real impedance, Z_r with the horizontal and vertical axes having the same scale, the bulk resistance, R_b for all samples can be obtained. When ever R_b was difficult to obtain from the complex impedance data, the impedance data were converted into admittance data and plotted according to the admittance formalism from which $1/R_b$ may be easier to obtain.[30] Table 6 shows the data (R_b and thickness, t) for all thin film samples.

The ionic conductivity at room temperature (r.t.) for all samples is illustrated in Figure 2. It depends on several factors, such as ionic dopant concentration, cationic or anionic type charge carriers, the charge carriers' mobility and the temperature. From the plot, it can be found that the conductivity of **K0** (chitosan-acetate) sample is at 6.80 ×

Table 5 Analytical data (%)* of **1–5**

Compound	C	H	N	S
1	60.32 (59.88)	5.87 (5.79)	10.42 (10.48)	8.12 (7.99)
2	60.84 (60.75)	6.39 (6.07)	10.08 (10.12)	7.88 (7.72)
3	61.66 (61.52)	6.38 (6.34)	9.89 (9.78)	7.68 (7.47)
4	62.76 (62.28)	6.70 (6.59)	9.51 (9.47)	7.47 (7.23)
5	63.11 (63.05)	6.92 (6.83)	9.42 (9.19)	7.04 (7.01)

*Theoretical values in brackets.

Table 6 The values (R_b and thickness, t) obtained for thin films

Sample	R_b	t (cm)
K0	2.13×10^6	0.006
K1	2.25×10^6	0.007
K2	1.50×10^6	0.012
K3	8.33×10^5	0.008
K4	7.50×10^5	0.009
K5	6.88×10^5	0.010

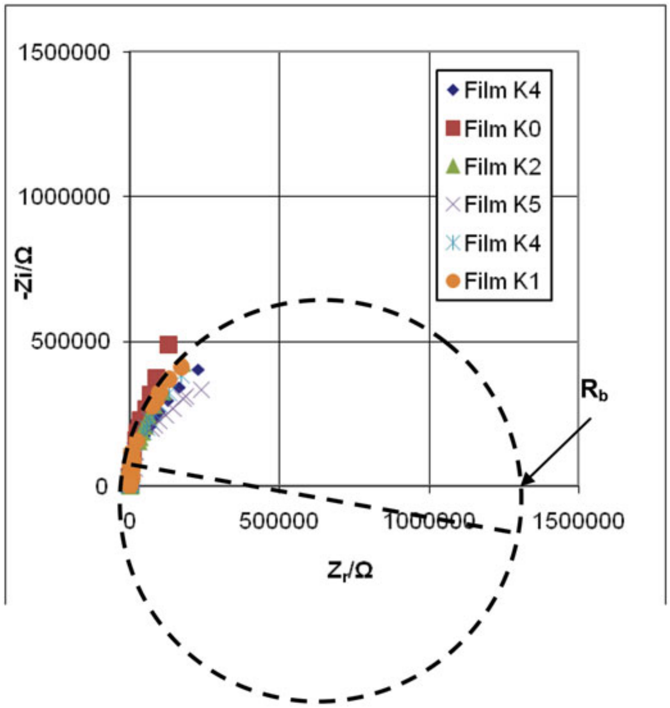


Figure 1 The $R_b$value obtained from the Cole–Cole Plot and the Cole–Cole Plot of all of the samples obtained using EIS.

10^{-10} S cm^{-1} and its show a similar range for pure chitosan film which has been reported.[31] Therefore, it was used as polymer host in this work to observe any changes of conductivity by addition of several types of thiourea compound. It can be seen, with the addition of nitrobenzoylthiourea, the ionic conductivity of thin films was found to be increased and the highest conductivity was observed for sample **K5** with the value 3.50×10^{-9} S cm^{-1}. The highest value of conductivity for sample **K5** due to the increased of length of the alkoxy (donor) group as shown from the previous study for compound **5**, thus the conductivity increases. Moreover, the molecular weight of the sample also gives the significant result to the conductivity as an increase of the molecular weight enhances the conductivity. This is supported by previous literature reports which claimed that as the amount of doping material (wt.%) increases, the conductivity of sample also increases.[32] Apparently, the conductivites of samples in this study increase as the length of alkoxy group in a sample increases with its molecular weight.

The results show that nitrobenzoylthioureas are very promising potential candidates to be used as molecular wires due to their π-conjugation system and charge carriers of the compound.[33]

CONCLUSIONS

Linear conjugated organic compounds A-ArC=ONHC=SNHAr-D [*N*-alkoxyphenyl-*N*′-(4-nitrobenzoyl)thioureas] have been successfully designed, prepared,

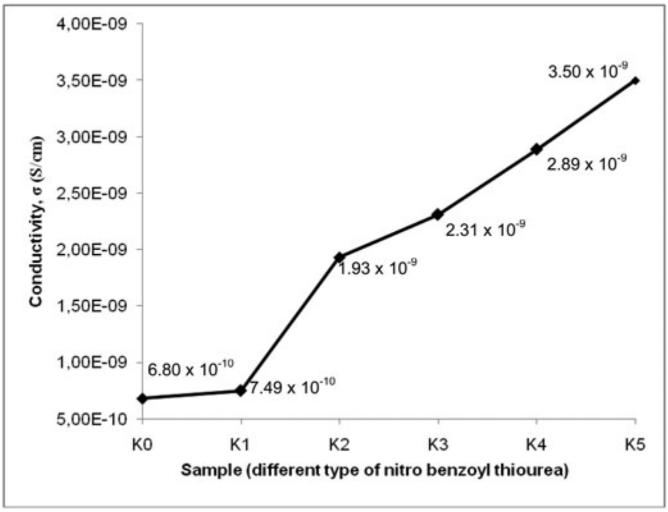


Figure 2 The ionic conductivity of thin films at room temperature (r.t.).

and characterized prior to form conductive thin film. All compounds were spectroscopically and analytically characterized by ^{1}H and ^{13}C NMR, FT-IR, UV-vis spectroscopy. The conductivity behavior of the compounds was revealed by using Electrical Impedance Spectroscopy (EIS). Data from EIS show an increase as the molecular weight of the samples increase as well as the length of the alkoxy group. This demonstrates that these compounds are promising candidates and exhibit great potentials to be explored and used as molecular wires in numerous microelectronics applications in the future.

EXPERIMENTAL

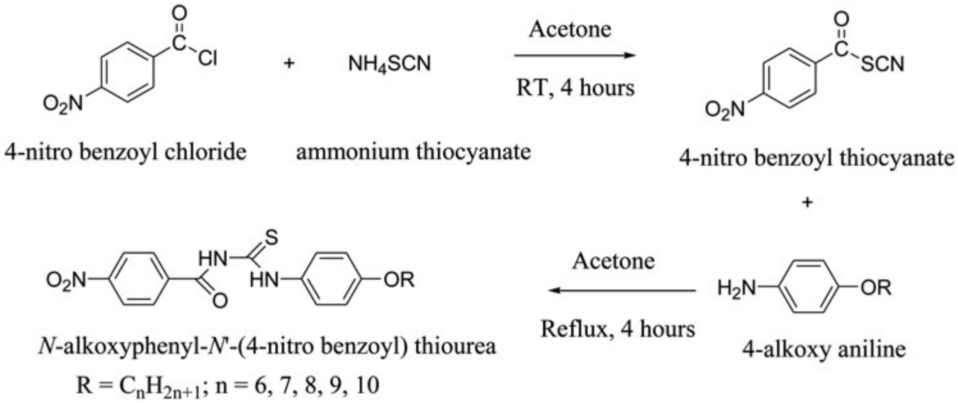
Materials and General Methodology

All reactions were carried out under an ambient atmosphere and no special precautions were taken to exclude air or moisture during work-up. ^{1}H (400.11 MHz) and ^{13}C (100.61 MHz) NMR spectra were recorded by use of a Bruker Avance III 400 Spectrometer with $CDCl_3$ as solvent and internal standard at r.t. in the range between δ_H 0–15 ppm and δ_C 0–200 ppm, respectively. IR spectra in the spectral range of 4000–400 cm^{-1} were recorded on KBr pellets using a FT-IR Perkin Elmer 100 spectrophotometer. UV-vis spectra were recorded with a Shimadzu UV-vis 1601 spectrometer by use of a 1 cm^3 cuvette in CH_2Cl_2 as solvent. Finally, the sample that form in thin films state were then characterized via EIS using a HIOKI 3532-Z LCR in the range 50 Hz–1 MHz in order to calculate the conductivity.

General Synthesis

The synthesis of the nitrobenzoylthiourea involved a reaction between 4-nitrobenzoyl chloride and ammonium thiocyanate with 4-alkoxyaniline at reflux for ca. 4 h. The reaction was carried out in acetone to give a yellow solution with a white precipitate of the inorganic salt as byproducts. After completion, the reaction mixture was cooled to r.t.

and filtered. The yellow filtrate was cooled with three ice cubes and filtered to obtain the *N*-(4-alkoxyphenyl)-*N*′-(4-nitrobenzoyl)thioureas as yellow solids with moderate yields (34–54%). For 4-alkoxyanilines, they have been reported in previous occasions[34,35] and characterization results have been referred. Scheme 1shows the synthetic approach applied in this study.



Scheme 1

N-[4-(Hexyloxy)phenyl]-*N*′-(4-nitrobenzoyl)thiourea (1)

A suspension of 4-nitrobenzoyl chloride (1.81 g, 9.7 mmol) in 50 mL acetone was added to ammonium thiocyanate (0.74 g, 9.7 mmol) in 50 mL of acetone to give a pale yellow solution and a white precipitate. The solution was stirred at r.t. for ca. 4 h before 4-(hexyloxy)aniline (1.87 g, 9.7 mmol) was added. After stirring for another ca. 4 h, the color of the solution turned from pale yellow to bright yellow. After adjudged completion by TLC (hexane/DCM = 4:6), the reaction mixture was cooled to r.t. and filtered. The yellow filtrate was cooled with three ice cubes and filtered to obtain yellow precipitate. The yellow precipitate was then recrystallized from MeOH to afford the title compound **1** (2.08 g, 54%).

N-[4-(Heptyloxy)phenyl]-*N*′-(4-nitrobenzoyl)thiourea (2)

Compound **2** (3.05 g, 34%) was prepared from 4-nitrobenzoyl chloride (4.01 g, 2.16 mmol), ammonium thiocyanate (1.65 g, 2.16 mmol), and 4-(heptyloxy)aniline (4.47 g, 2.16 mmol) as described above.

N-[4-(Octyloxy)phenyl]-*N*′-(4-nitrobenzoyl)thiourea (3)

Compound **3** (4.50 g, 49%) was prepared from 4-nitrobenzoyl chloride (4.01 g, 2.16 mmol), ammonium thiocyanate (1.64 g, 2.16 mmol), and 4-(octyloxy)aniline (4.79 g, 2.16 mmol) as described above.

N-[4-(Nonyloxy)phenyl]-*N′*-(4-nitrobenzoyl)thiourea (4)

Compound **4** (5.14 g, 54%) was prepared from 4-nitrobenzoyl chloride (4.07 g, 2.16 mmol), ammonium thiocyanate (1.64 g, 2.16 mmol), and 4-(nonyloxy)aniline (5.08 g, 2.16 mmol) described above.

N-[4-(Decyloxy)phenyl]-*N′*-(4-nitrobenzoyl)thiourea (5)

Compound **5** (3.52 g, 36%) was prepared from 4-nitrobenzoyl chloride (4.08 g, 2.16 mmol), ammonium thiocyanate (1.65 g, 2.16 mmol), and 4-(decyloxy)aniline (5.39 g, 2.16 mmol) as described above.

Thin Film Preparation

The thin films were prepared by the solution casting technique. 2 g Chitosan (Eastern Global) which was used as the polymer host was dissolved in 100 mL of 1% acetic acid solution. Then, different (nitrobenzoyl)thioureas in 0.4 wt.% o were added separately into the chitosan solution. The mixture was continuously stirred until the complete dissolution of the (nitrobenzoyl)thiourea. The mixture was then poured into different Petri dishes and left dried at ambient temperature for film formation. The films were kept in desiccators for further drying before characterized to ensure no water present. Table 7 shows the composition and designation of the thin film.

Electrical Conductivity Measurement

In order to investigate the ionic conductivity of the chitosan-(4-nitrobenzoyl)thiourea based thin films, the impedance spectroscopy was performed. The biodegradable films were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrolytes under spring pressure (as shown in Figure 2). The samples were characterized via EIS using HIOKI 3532–50 LCR Hi-Tester interfaced to a computer in a frequency range between 50 Hz and 1 MHz. The conductivity σ of the film can be calculated from the equation:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

Table 7 Composition of the thin films

Designation	Chitosan (g)	Volume of 1% acetic acid (ml)	Weight of dopant (sample) (g)
K0	2	100	—
K1	2	100	0.4 wt.% of 1
K2	2	100	0.4 wt.% of 2
K3	2	100	0.4 wt.% of 3
K4	2	100	0.4 wt.% of 4
K5	2	100	0.4 wt.% of 5

Here, A (cm^2) is the electrode–electrolyte contact area of the film and t its thickness. R_b is the bulk resistance obtained from the complex impedance plot (Cole–Cole plot) at the intersection of the plot and the real impedance axis.

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