



Synthesis and fluorescent properties of 2,3-dimethylquinoxaline substituted poly(phenylenevinylene) oligomer via Wittig reaction

R.Padma, S.Guhanathan*

PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous),
Vellore, Tamilnadu, (INDIA)
E-mail: sai_gugan@yahoo.com

ABSTRACT

Fluorescent heterocyclic compounds are of immense interest as functional materials in the emitters of electroluminescence devices and in the molecular probes used for biochemical research as well as in the traditional textile applications. Organic π -conjugated polymers are much academic and significant technological interest due to their optical and electronic properties. Of these materials, poly(phenylenevinylene)s (PPVs) have attracted the most attention and found greatest utility in electronic devices. In addition, the presence of electron withdrawing N-heterocycles such as pyrazine and quinoxaline rings to be used as electron-attracting part in π -conjugated structures. Poly(p-phenylene vinylene) are one of the most important classes of conjugated polymers, with a wide range of applications, such as light-emitting diodes, optoelectronic devices etc. Hence, the present investigation was devoted to the synthesis of phenylenevinylene oligomer substituted quinoxaline derivatives using 2,3-dimethylquinoxaline with terephthalaldehyde via Wittig reaction. The structures of synthesised compounds were confirmed by FT-IR, ^1H , ^{13}C , ^{31}P -NMR spectral data. The results of fluorescent experiment on the synthesised compound found to exhibit the photoluminescence with bluish green emission maxima at shorter wavelengths of 460nm.

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KEYWORDS

Pyridinylthiadiazole;
Triazolylthiadiazole;
Indolylthiadiazole;
Quinazolinonylthiadiazole.

INTRODUCTION

π -Conjugated oligomers^[1] like oligo(phenylenevinylene)s^[2,3] and their heterocyclic derivatives^[4-7] have attracted much interest for the application as an active material in organic light-emitting devices. Large numbers of different classes of light-emitting conjugated polymers have been developed, e.g., poly(carbazole)s, poly(fluorine)s (PFs), PPVs, poly(phenylene vinylene)s, and

poly(thiophene)s (PTs). While PPV and its derivatives are still the leading materials for green-light-emitting PLEDs, the larger-bandgap PFs are the top polymeric blue-light emitters^[8]. The organic materials are used in the construction of photoelements, capacitors, diodes, batteries, chemical sensors, polymer lasers, NLO devices and transistors^[9]. One of the fastest developing disciplines is the electroluminescence (EL) of organic compounds. Quinoxaline, also called benzopyrazine is a heterocyclic com-

pound containing a ring complex made up of a benzene ring and a pyrazine ring^[10]. Pyrazines and Quinoxaline derivatives exhibit a large range of biological activities and used for pharmaceuticals or phytosanitary applications^[11]. Besides their medicinal uses, pyrazine and Quinoxaline derivatives have found technical applications as dyes, electroluminescent materials, organic semi-conductors and as suitable ligand in coordination chemistry.

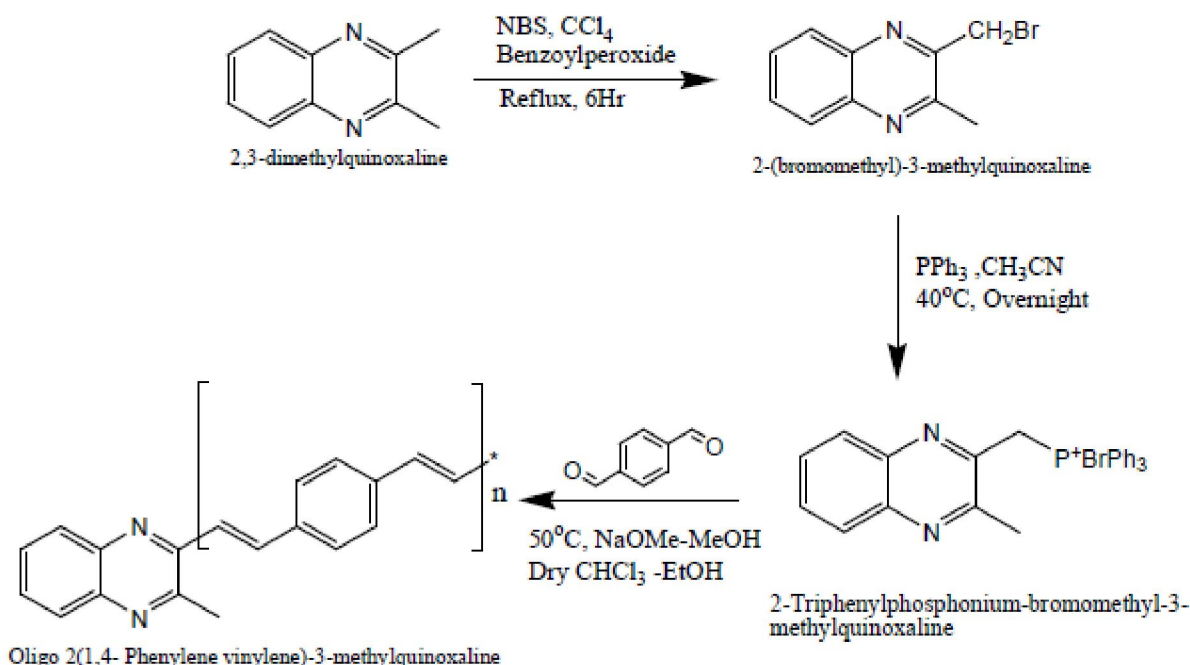
The synthesis of extended π -Conjugated systems has been the key to provide organic materials with such properties. These compounds are often based on a push-pull system, which is constituted by an electron-donating group (D) and an electron-withdrawing group (A) linked through a π -Conjugated spacer. The molecular properties of the chromophores depend on the strength of the "push-pull" effects which are function of the ability of the donor to provide electrons and the acceptors to withdraw electrons. Pyrazine and Quinoxaline, which are highly π -deficient aromatic heterocycles, can be used as electron withdrawing part in push-pull structures for intramolecular charge transfer (ICT). Such important ICT along the backbone of the molecule can induce luminescence properties. The ability of protonation, hydrogen bond formation and chelation of the nitrogen atoms of the 1,4-diazine ring are also of great importance, such derivatives could be therefore used

for the formation of supramolecular assemblies and used as sensors^[12]. Based on the careful analysis of literature, there was limited number of reports on benzopyrazine based PPV^[13-16]. Hence, the present investigation was aimed to synthesis benzopyrazine based PPV and their detailed characterisation.

MATERIALS AND METHODS

The chemicals 2,3-butadiene, ortho-phenylenediamine, N-Bromosuccinimide, Benzoylperoxide, Tri-phenylphosphine, terephthalaldehyde were purchased from Avra, Chennai, India. Silica gel (TLC and Column grade) were purchased from Merck. Methanol, ethanol, acetone, chloroform, acetic acid, acetonitrile were purchased from S.d fine-Chem, India and solvents were purified by according to standard procedure. UV spectra were also recorded using Alpha Bruker UV spectrophotometer. FTIR spectra were recorded in KBr disk on a Alpha Bruker FTIR spectrophotometer. ¹H, ¹³C, & ³¹P NMR was assayed using Bruker Advanced 300MHz NMR spectrometer, TMS was used as internal standard and CDCl₃, DMSO as solvent. PL studies were done by using spectrofluorometer FP-8500, JASCO.

SCHEME OF THE REACTION



EXPERIMENTAL

a) Synthesis of 2-bromomethyl-3-methylquinoxaline.

2,3-dimethylquinoxaline (1.58g, 0.01mol) and NBS (1.80g, 0.01mol) were refluxed overnight in 30ml CCl_4 containing 0.08g (0.0003 mol) benzoyl peroxide. The by product NBS was removed by filtration. The reaction medium was washed with CCl_4 and the solvent evaporated.

b) 2-Triphenylphosphonium-bromomethyl-3-methylquinoxaline

2-bromomethyl-3-methylquinoxaline(0.59g,

2.5mmol) and triphenylphosphine (2.8g, 10.5mmol) was dissolved together in acetonitrile(20ml). The solution was stirred overnight at 40°C. The resulting precipitate was recrystallized from toluene-methanol mixture (2:1) to yield phosphonium ylide compound.

c) Oligo 2(1,4- Phenylene vinylene)-3-methylquinoxaline

The phosphonium salt (0.50g, 1mmol) and terephthalaldehyde (0.27g, 2mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12ml, 3+1 v/v) under N_2 atmosphere. Then, a predetermined amount of sodium methoxide

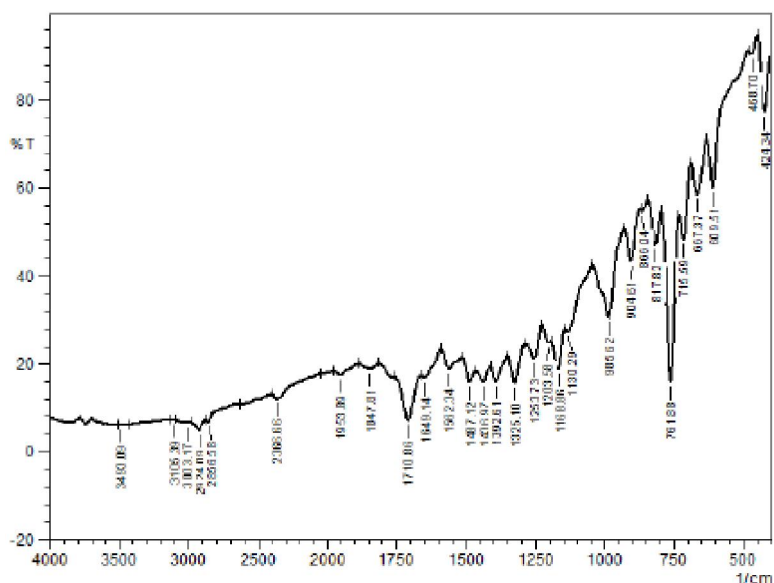


Figure 1 : FT-IR spectrum of 2-bromomethyl-3-methylquinoxaline

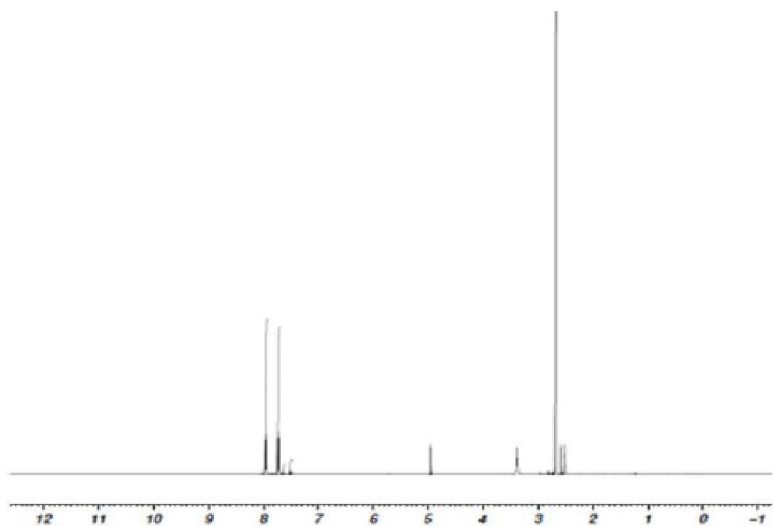


Figure 2 : ^1H NMR spectrum of 2-bromomethyl-3-methylquinoxaline

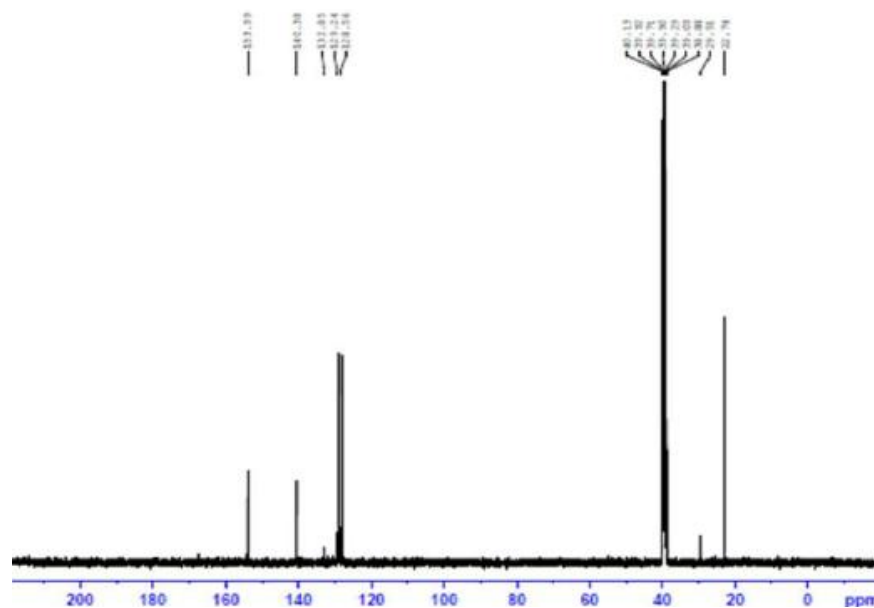


Figure 3 : ^{13}C NMR spectrum of 2-bromomethyl-3-methylquinoxalin

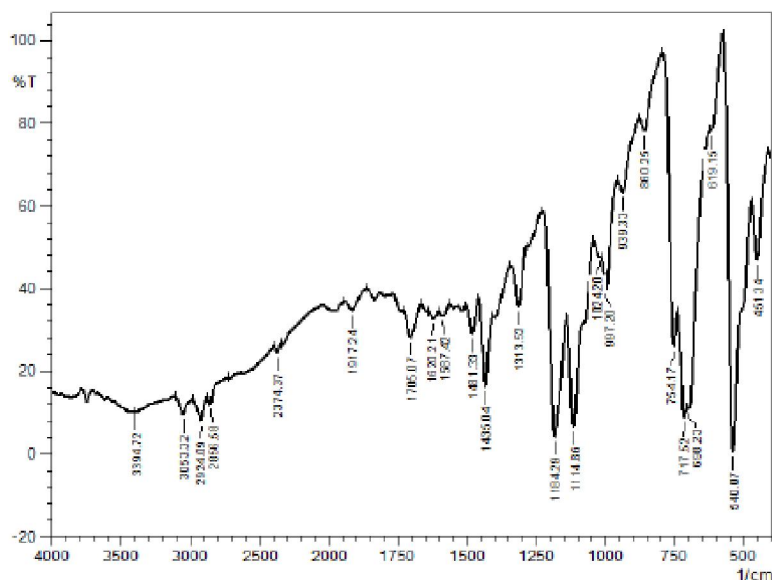


Figure 4 : FT-IR spectrum of 2-Triphenylphosphonium-bromomethyl-3-methylquinoxaline

(25wt% in methanol, 1.3ml, 5.6mmol) was added and the resulting solution was stirred at 50°C overnight. Precipitation in methanol gave oligomer, which was reprecipitated from Dichloromethane-methanol. Formed oligomer was purified by dissolving in acetonitrile and chloroform.

RESULTS AND DISCUSSION

2-bromomethyl-3-methylquinoxaline

FT-IR (KBr, cm^{-1}): 2924.09 (C-H, st), 1325.10 (C-N, st), 1487.12 (C=N, st), 761.88 (C-Br, st)

$^1\text{H-NMR}$ (DMSO, ppm): 2.678 δ (3H, s) 4.959 δ (2H, s) 7.731 δ (2H, q) 7.969 δ (2H, q)

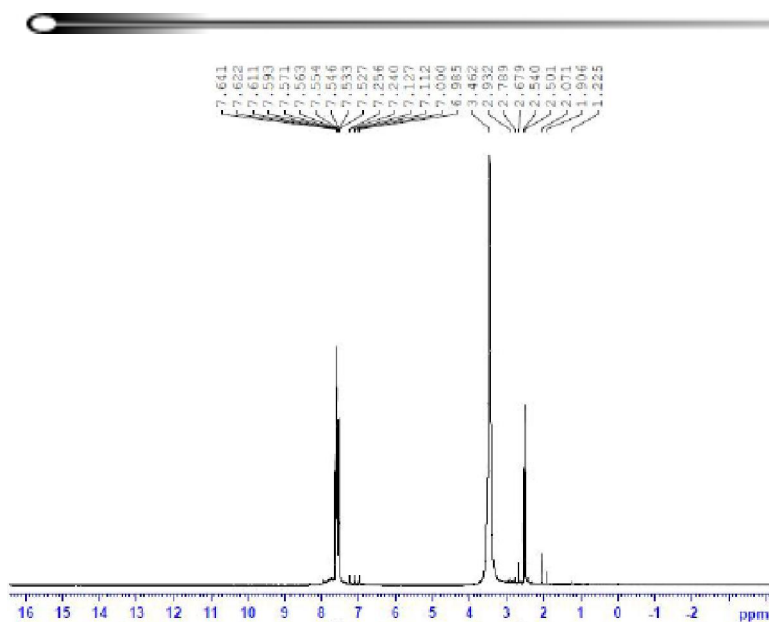
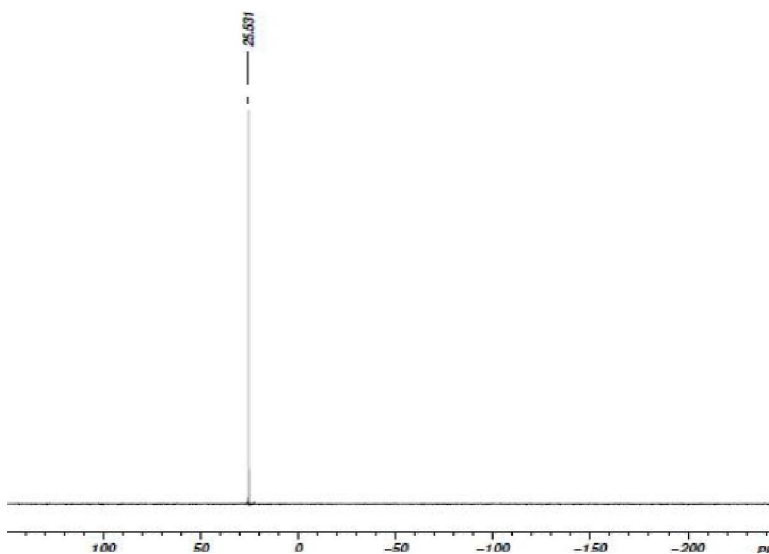
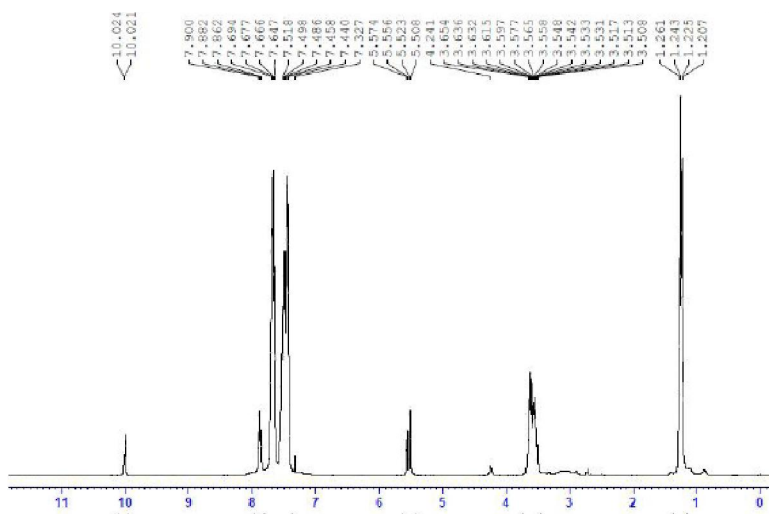
$^{13}\text{C-NMR}$ (DMSO, ppm): 22.74 δ , 29.51 δ , 128.56 δ , 129.24 δ , 140.38 δ , 153.99 δ .

2-Triphenylphosphonium-bromomethyl-3-methylquinoxaline

FT-IR (KBr, cm^{-1}): 2924.09 (C-H, st), 1313.52 (C-N, st), 1705.07 (C=N, st), 698.23 (C-P, st), 754.17 (C-Br, st), 540.07 (P-Br, st)

$^1\text{H-NMR}$ (DMSO, ppm): 1.225 δ (3H, s), 2.679 δ (2H, s), 7.533 δ (15H, s), 7.641 δ (4H, m)

$^{31}\text{P-NMR}$ (DMSO, ppm): 25.531 δ (1P, s)

Figure 5 : ^1H NMR spectrum of 2-triphenylphosphonium-bromomethyl-3-methylquinoxalineFigure 6 : ^{31}P NMR spectrum of 2-triphenylphosphonium bromomethyl-3-methylquinoxalineFigure 7 : ^1H NMR spectrum of Oligo 2(1,4-Phenylene vinylene)-3-methylquinoxaline

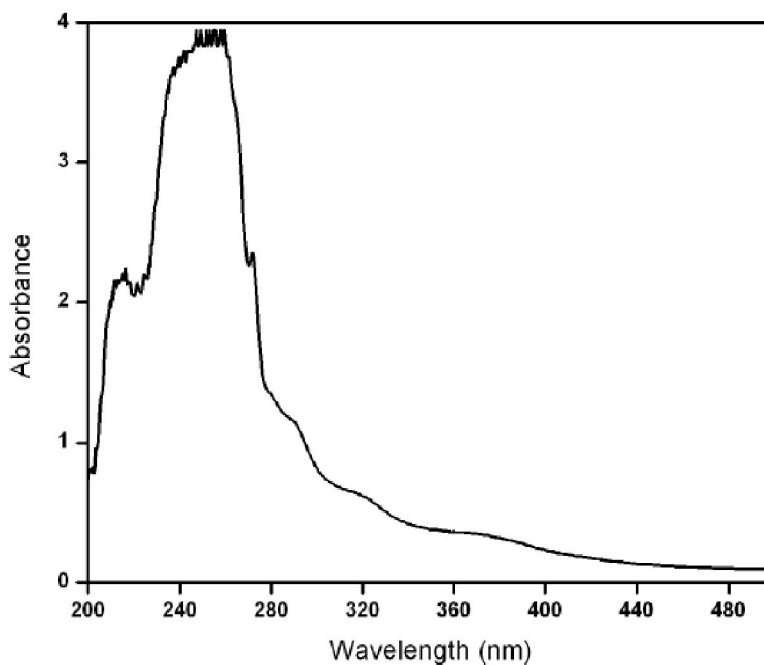


Figure 8 : UV-VIS spectrum of oligo 2(1,4-phenylenevinylene) 3-methylquinoxaline

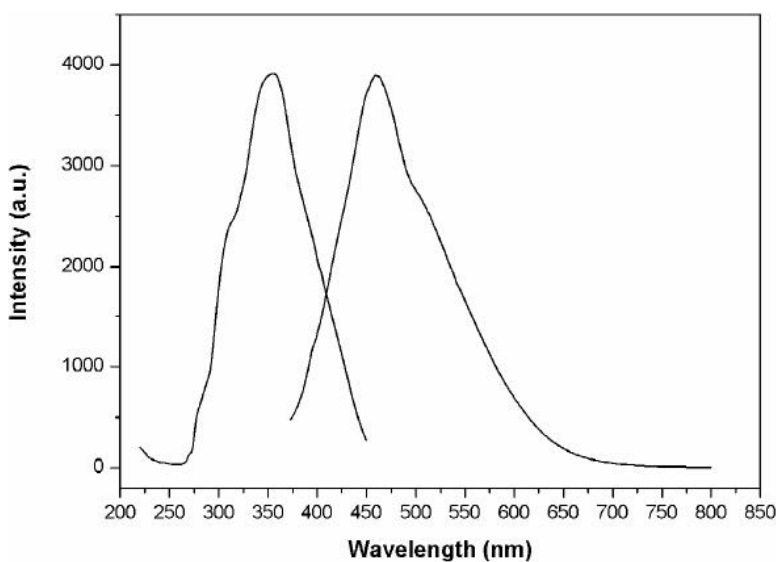


Figure 9 : PL spectrum of oligo 2(1,4-phenylenevinylene)3-methylquinoxaline

Oligo 2(1,4- Phenylene vinylene)-3-methylquinoxaline

$^1\text{H-NMR}$ (CDCl_3 , ppm): 1.225 δ (3H, s) 3.615 δ (1H, d) 5.508 δ (1H, d) 7.440 δ (2H, t) 7.647 δ (2H, t) 10.021 δ (4H, s)

NMR , $^{31}\text{P-NMR}$ spectral studies. Photoluminescent property of the synthesized oligomer was investigated using uv-vis and spectrofluorometer. The PPV oligomer showed the photoluminescence with bluish green emission at 460nm.

CONCLUSIONS

Quinoxaline based PPV oligomer has been synthesized using Wittig reaction. Formation of the oligomer was confirmed with FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$

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