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Synthesis and characterization new tetra-3-chlorobenzothiophene-[1,3,4]-oxadiazole appended metallophthalocyanines for dielectric studies

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ABSTRACT

New 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines have been efficiently synthesized by the reaction of tetracarboxy metallophthalocyanines with 3-chlorobenzothiophene acid hydrazide. The structural integrity of the peripherally substituted metallophthalocyanine complexes were elucidated by elemental analyses, FT-IR, solid state electronic absorption spectroscopy and solid state ^{13}C *NMR spectroscopy. In addition, powdered X-ray diffraction (XRD) and thermo gravimetric analysis (TGA) were also performed to realize crystallographic nature and thermal stability. Further the dielectric constant* (ε^1) *and AC conductivity* (σ_{ac}) *of BTHPcs was also studied. The variation of capacitance* (C_s)*, loss tangent* ($\tan\delta$) *and impedance (Z) with frequency range of 50 to* $5x10^6$ *Hz was observed at room temperature and it clearly shows that all these complexes carousing that non-Debye type relaxation caused by hopping charges may relevant for the dielectric responses.*

Keywords: Substituted metallophthalocyanines, benzothiophene [1,3,4]-oxadiazole, solid-state electronic absorption spectra; solid-state ^{13}C-NMR, dielectric constant, AC conductivity.

INTRODUCTION

The research and development in metallophthalocyanines (MPcs) has progressively become dominated by their fascinating unique properties like high thermal stability, chemical resistance and their conjugated π-system. Consequently, variety of MPcs have been synthesized and explored for their feasible applications in dye sensitized solar cells and photovoltaic cells [1, 2] as colorants [3], semiconductors and photoconductors [4, 5], photocatalysts [6], chemical sensors [7, 8], photosensitizers [9], nonlinear optics [10], liquid crystals [11, 12] and they still have many other potential applications both in biomedical and materials research. Derivatives of 1,3,4-oxadiazoles are important class of heterocyclic compounds which demonstrate a wide range of pharmaceutical and technological applications. As a consequence of the electron deficiency, high thermal and oxidative stability, 1,3,4-oxadiazoles derivatives are widely used as electron transporting and hole blocking materials in organic light emitting devices (OLEDs). MPcs and metal porphyrins are well known transition metal macrocyclic complexes which exhibit high dielectric constant. Many reports are documented for the development of high dielectric constant polymer composites involving MPcs [13-17] and as well as our group recently synthesized 1,3,4-oxadiazole substituted MPcs derivatives exhibited exhibited acute electronic interaction, excellent thermal stability and electrical conductivity properties [18, 19]. The literature survey reveals that, no data has been reported by using of thiophene, containing heterocyclic substituted MPcs via 1,3,4-oxadiazole bridge. thiophene, a sulfur-containing aromatic heterocycle, can posseses remarkable electrochemical and optoelectrical properties. Due to their various potential applications in a wide range of the organic electronic devices [20, 21], thiophene derivatives have become major components or key precursors for the design and synthesis of novel materials. In continuation of our quest to design, synthesize and study π-expanded phthalocyanines systems, we planned to introduce an oxygen, nitrogen and sulfur containing heterocyclic benzothiophene and 1,3,4-oxadiazole moieties onto periphery of electron-rich Pc ring system, consequently in this work, we have undertaken the synthesis of the benzothiophene heterocyclic appended MPcs judging from the ease of synthetic route. The present report describes the synthesis and characterization of benzothiophene appended metal phthalocyanines and demonstrated improved optical absorption by absorbing broad spectral range in the visible spectrum region, clubbed with excellent thermal and chemical stability. AC conductivity studies were performed and results were discussed.

MATERIALS AND METHODS

Materials and Equipment

Cinnamic acid and thionyl chloride were purchased from sigma aldrich and used without further purification. All other chemicals used were of reagent grade quality. The solvents were dried over molecular sieves of 4°A. Polyphosphoric acid (PPA) and hydrazine hydrate were obtained from spectrochem chemicals and used as received. 3-chlorobenzothiophene hydrazide [22] and 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines were synthesized as per the known procedure [18, 19]. All the synthesized final compounds were characterized with Infrared spectra were recorded using FT-IR 8400s Shimadzu spectrometer with KBR pellets in the range of 400-4500 cm^{-1}. The elemental analysis was performed using Carlo-Erba 1106 instrument, The UV/Vis-35. The H^1 NMR spectra recorded on USA^{1}H 400 MHz Varian-AS NMR spectrometer using TMS as an internal standard and the solid state ^{13}C-NMR spectra were recorded on Bruker DSX-300 solid-state NMR spectrometer with a magnetic field of 7.04T and carbon frequency of 75.47MHz (internal standard was glycine). Mass spectra were recorded with a LC-MSD-trap-XCT plus mass spectrometer. Thermal analysis was carried out in SHIMDAZU TA-60WS thermal analyzer in air at a heating rate of 5°C min^{-1}, Powdered X-ray measurements were carried out on a D8 Advance X-ray Diffractrometer. Electrical measurements were carried out using following devices fabricated in a sandwich configuration Ag/Polymer/Ag with powdered 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPcs samples compressed into pellets and conducting silver paint (ELTECKS preparation No. 1228–C) was coated on both flat surfaces of the pellets and the electrical contacts to the samples were made using the same silver paint to the electrodes. The electrical contacts were checked to verify the ohmic connection. The dielectric and AC electrical conductivity measurements were carried out by the two probe method using a Hioki 3522-50 and 3532-50 LCR HiTester. Devices were fabricated in sandwich configuration Ag/Mpc/Ag with powder samples of the phthalocyanines into pellets and conducting silver paint (eletecks preparation No 1228-C) was coated both flat surface of the pellets and electrical contact on were checked to verify ohmic connection, Dielectric constant, loss of tangent, capacitance and Ac conductivity measured.

Synthesis

General route for the preparation of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines was carried out by the condensation and cyclization followed was apprehended in the presence of polyphosphoric acid . Tetracarboxy MPcs (0.001 mol) and 3-chlorobenzothiphene hydrazide (0.006 mol) were added successively with stirring to dry polyphosphoric acid. After the homogeneous mixing, the reaction mixture was stirred at 150°C for 24 hour. The reaction mixture was poured into 200mL of ice cold water and stirred for 20 min. The precipitate was filtered off, and washed several times with cold water until the filtrate became neutral. After drying in vacuum at 50°C, the crude product was purified with 0.1 N sodium hydroxide solution followed by water, hot acetic acid, 10% sodium bicarbonate solution, obtained final compound is insoluble in all organic solvent.

3-chlorobenzothiophene-1,3,4-oxadiazole substituted nickel phthalocyanine (NiBTHPc)

Yield: 92%; Anal. Calcd. for $C_{72}H_{28}Cl_4N_{16}NiO_4S_4$: C, 56.57; H, 1.76; Cl, 8.92; N, 13.94; Ni, 3.46; O, 3.94; S, 8.49%. found: C, 57.27; H, 1.87; Cl, 9.39; N, 14.84; Ni, 3.89; O, 4.24; S, 7.98%; IR= [(KBr) ν_{max}/cm^{-1}]: 3065 (Ar-CH), 2922 (Ar-CH), 2848 (Ar-CH), 1560.41 (C=N), 1 430 (C=C), 841 (C-S-C), 1082.88 (C-Cl), 889.89, 824, and

724 (Pc skeleton vibration. ^{13}C NMR (Solid State) δ/ppm BTPc, 120-150(Pc Core), 160-180 (benzothiophene moiety), 210-240 (oxadaizole ring).

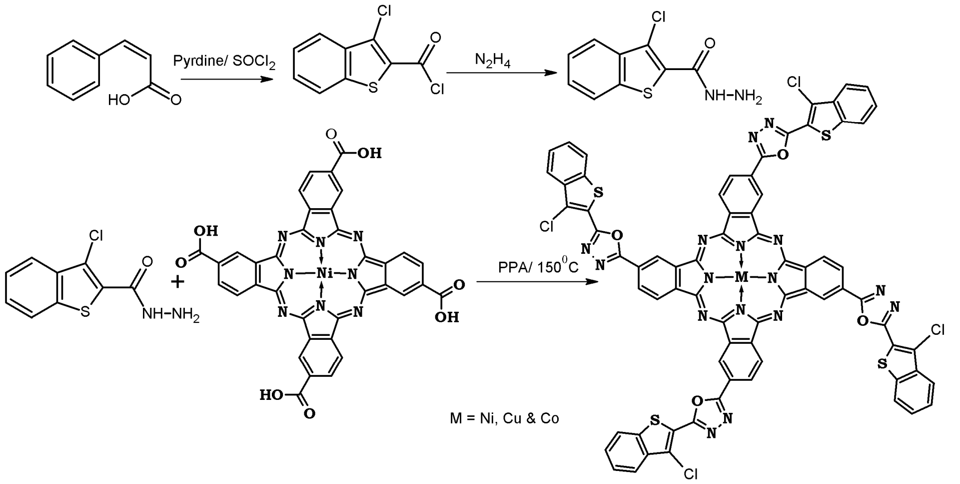
3-chlorobenzothiophene-1,3,4-oxadiazole substituted copper phthalocyanine (CuBTHPc)
Yield: 91%; Anal. Calcd. for $C_{72}H_{28}Cl_4CuN_{16}O_4S_4$: C, 57.09; H, 1.81; Cl, 9.36; Cu, 4.20; N, 14.23; O, 3.91; S, 8.47%. found: C, 56.87; H, 1.46; Cl, 8.95; Cu, 3.92; N, 14.80; O, 4.23; S, 7.97%; IR= [(KBr) ν_{max} /cm^{-1}]: 3054 (Ar-CH), 2895 (Ar-CH), 2838 (Ar-CH), 1560.14 (C=N), 1435 (C=C), 839 (C-S-C), 1082.88 (C-Cl), 889.87, 825, and 722 (Pc skeleton vibration),

3-chlorobenzothiophene-1,3,4-oxadiazole substituted cobalt phthalocyanine (CoBTHPc)
Yield: 93%; Anal. Calcd. for $C_{72}H_{28}Cl_4CoN_{16}O_4S_4$: C, 57.27; H, 1.87; Cl-9.36; Co, 3.90; N, 14.74; O, 3.88, S, 8.49 %. found: C, 56.97; H, 1.72; Cl, 9.25; Co, 3.70; N, 14.88, O, 4.16; S, 8.35%; IR= [(KBr) ν_{max} /cm^{-1}]: 3054 (Ar-CH), 2895 (Ar-CH), 2838 (Ar-CH), 1566.16 (C=N), 1435 (C=C), 839 (C-S-C), 1082.88 (C-Cl), 932.78, 889.89, 825, and 729 (Pc skeleton vibration)

RESULTS AND DISCUSSION

Synthesis

Finely ground mixture of tetracarboxy MPcs (0.001 mol) and 3-chlorobenzothiophene hydrazide (0.006 mol) were suspended and stirred in to 100 g preheated (120 °C) polyphosphoric acid (PPA) containing 10 g of P_2O_5 in 100mL round bottom flask provided with a mechanical stirrer and was maintained at 150 °C for 24 h, synthetic route is as shown in Scheme 1. The reaction mixture was allowed to cool and was quenched with ice cold water and filtered. The obtained crude product was repeatedly treated with 0.1 N sodium hydroxide solution followed by water, hot acetic acid, 10% sodium bicarbonate solution, water and acetone to get 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines.



Scheme 1: the synthesis of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines

Newly synthesized 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPc complexes were characterized by elemental analysis, FT-IR, solid-state UV-Vis, solid-state ^{13}C-NMR spectroscopy, thermal analyses and XRD studies. The infrared spectral data of the 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPcs are shown in Figure 1.

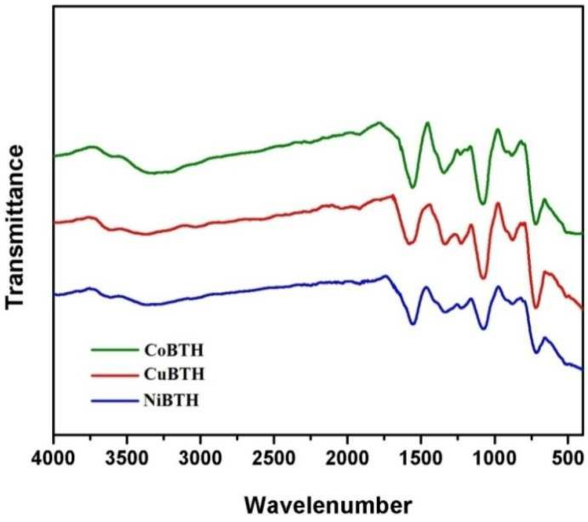


Figure 1: IR-spectra of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines

It can be observed that, the band appearing about 3404 cm^{-1} was assigned for presence of hydrogen of moisture absorbed on KBr pellets and observed in all three MPcs. One of the significant characteristic indications of condensation followed by cyclization reaction i.e. in the TCPNi 1692 cm^{-1} band disappeared in BTHPC these due to participation of COOH in cyclization reaction. A peak at 1560.41 cm^{-1} is assigned to C=N of imine group and peak at 1432 cm^{-1} can be assigned for C-N, 1345 cm^{-1} C=C in plane skeletal vibration of the Pc. the peaks at 1406.9-1325.4 cm^{-1} are due to C-H symmetric bending. The absorption bands appeared around 1090 cm^{-1} was assigned to C-Cl stretching and 889.89 cm^{-1} for C-S-C stretching frequency of the peripheral Substation o the ring. All other remaining series of absorption bands at 915.7, 841.8 & 432 cm^{-1} are attributed to the various skeletal vibration of PC ring. We did not investigate ^{1}H-NMR spectra of this final compound because of insolubility in all most all the organic solvent. Hence confirmed the proposed structures of the compound by solid state ^{13}C NMR spectra as shown on figure 2. Solid state ^{13}C NMR spectra of compound (NiBTHPc), exhibited the broad signal in the range of 120-150 ppm for the aromatic carbons phthalocyanine core and further peak at 160-180 ppm for aromatic carbon of benzothiophene moiety uniformly. And the electron deficient with oxadiazole moiety carbon appears at 210-240.

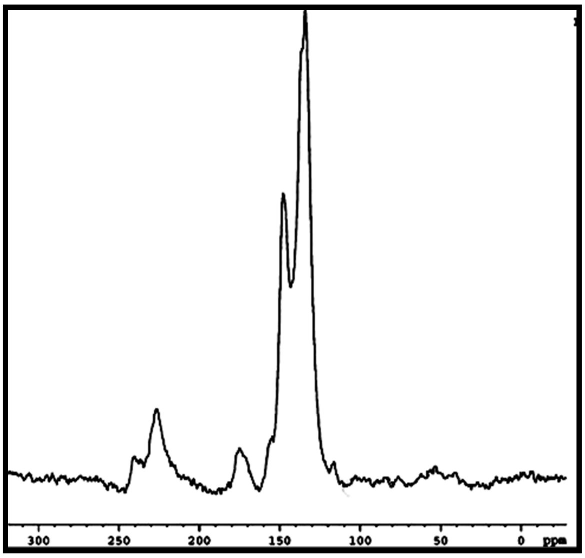


Figure 2: Solid-state 13C-NMR spectra of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted nickel phthalocyanines (NiBTHPc)

Electronic Absorption Spectra

Electronic absorption spectra shows are fruitful to establish the structure of Peripheral 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines and strong electronic absorption spectra and remarkable optical properties were represented in the figure 3. Solid state electronic absorption spectra dominated by two intense bands, the UV region within the range of 350–400 nm (Soret or B band) and the Q band around 600 in the visible region. Peripheral substitution of phthalocyanine shows hard splitting Q band can be observed is due to the Q band absorptions of MPcs complexes are due to $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{2-} ring because of transition indicate effective electronic transition between PC and peripheral moiety of the two ring arrangement of Pc core. On the other hand, their B band absorptions arise from the deeper π-levels →LUMO transitions.

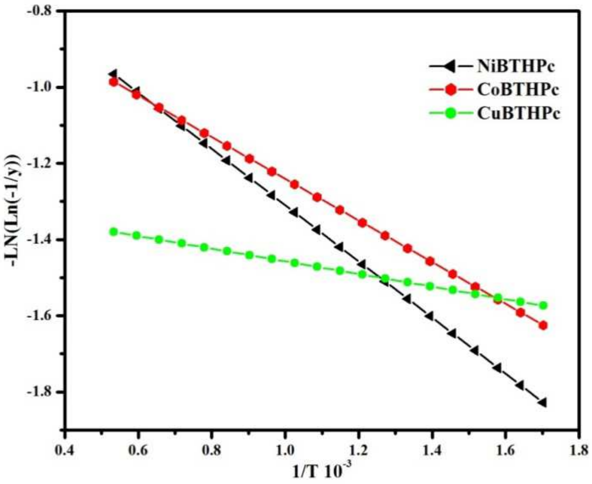


Figure 3: Solid-state electronic absorption spectra for 3-chlorobenzothiophene -1,3,4-oxadiazole substituted Metallophthalocyanines

Thermal Analysis

Thermo gravimetric curves of all metal phthalocyanines recorded as shown in figure 4, kinetic and thermodynamic parameters of decomposition was evaluated by using Broido's method. Initial step degradation observed at temperature region of 35-135^{0}C due to the moisture loss of weight was happened. leading decomposition start in between from 400 to to 520°C for (CoBTHPc), 390 to 520°C for (CoBTHPc), and 350 to 520°C for (NiBTHPc) respectively.

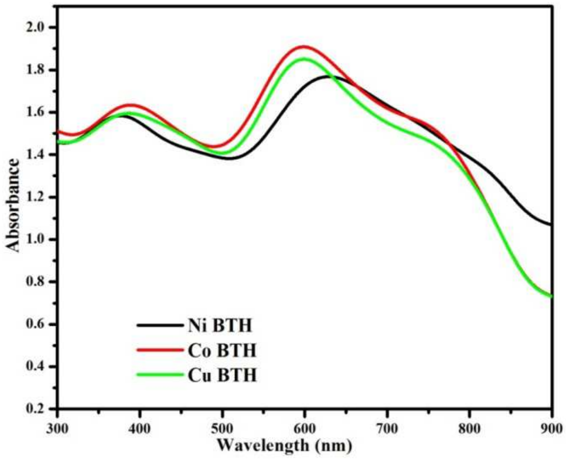


Figure 4: Plots of -ln (ln1/Y) versus 1/T for thermal degradation for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPcs from temperature range 350-520°C

Phthalocyanine compounds are shows degradation is associated with endothermic in nature of their decomposition and The thermal analysis yields the stability of MPcs complexes, all shows stability > 350 °C. The changes in entropy of activation are negative for all the compounds varied from -113 to 175 (kJmol^{-1}). From the plots, The degradation kinetic is evaluated by allowing for the sudden decreasing in weight of substance as a function of temperature, the activation energy (Ea) and frequency factor (ln A) were evaluated. The enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been computed using standard equations and are summarized in table 1.

Table 1: The loss of weight at the major decomposition temperature was 99% for Pc Thermodynamic parameters for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines

Pc compound	Temperature of decomposition(ºc)	DTA_{max} (ºc)	E_A (kJmol^{-1})	ΔH (kJmol^{-1})	ΔS (kJmol^{-1})	ΔG (kJmol^{-1})
NiBTHPc	350-520	430	0.01413	-6.6031	-160.09	113.38
CuBTHPc	360-520	440	0.01378	-6.0803	-161.47	114.35
CoBTHPc	360-520	425	0.01406	-6.0833	-159.76	112.94

XRD analysis

The powdered X-Ray diffraction study of NiBTHPc, CuBTHPc and CoBTHPc phthalocyanine were done in the range 2θ angles 3-60 as shown in the figure 5. The diffraction pattern of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPcs are show broad peaks with less intensity because of addition 3-chlorobenzothiophene-1,3,4-oxadiazole substituted in the phthalocyanine periphery and it causes conjugation and π-electrons manipulate the stacking arrangement and the shapes of the X-ray diffraction spectrograph indicate that these all three metals of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted phthalocyanines are in amorphous in nature.

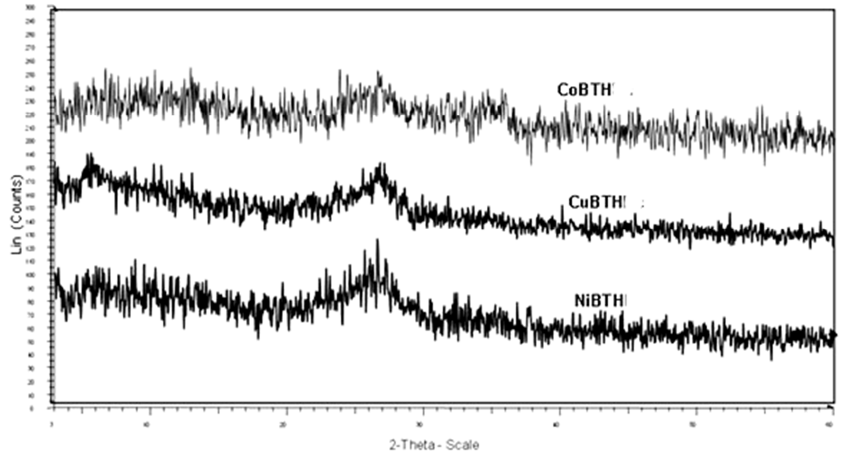


Figure: 5 Powder X-ray diffraction pattern for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines

AC Conductance as a function of frequency

Figure 6 shows the room temperature variation of AC conductance with frequency range from 50 Hz to 1 MHz employing an alternating voltage amid amplitude 1V peak-to-peak Results have been reported for pellets of MPcs materials maintained under vacuum. Its comprehensible from the plot that, Ac conductivity is frequency independent and plummets at sufficiently elevated frequency, it was well established method for characterizing by the contrary to band model, the predominance of the hopping dynamics of the charge carrier/ions up to the 1 MHz [23], all the substituted phthalocyanines complexes shows constant conductivity and at higher frequencies the conductivity increases linearly because of the substituent groups at the peripheral 3-chlorobenzothiophene-1,3,4-oxadiazole of the phthalocyanine molecule cause conjugation and π-electrons manipulate the differences in stacking arrangement and planar distances between the molecules. Among three complexes highest electrical conductivity was observed for nickel phthalocyanine complex was due to the smaller inter planar spacing between the molecule as well as favorable inter molecular stacking which were expected to lead to the greater π-electron interactions between the molecules resulting highest electrical conductivity and all the complexes shows non-Debye type relaxation caused by hopping type of conduction mechanism may be relevant for the dielectric response [24].

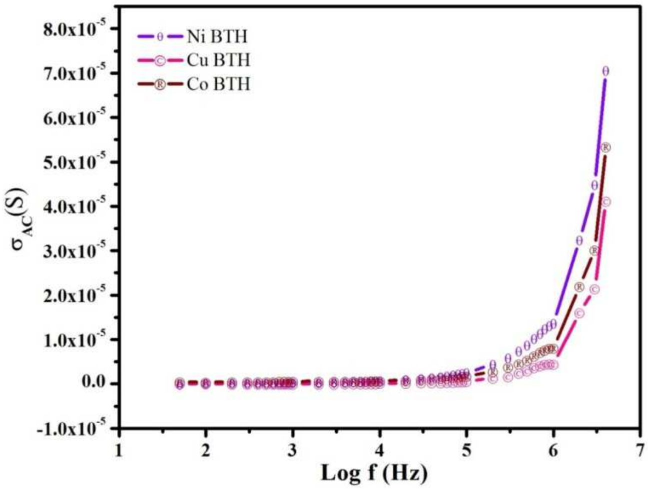


Figure: 6 Shows frequency dependence of the AC conductivity of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines at room temperature

Capacitance as a function of frequency

Variation of capacitance with frequency at room temperature of 3-chlorobenzothiophene-1,3,4-oxadiazole substituted MPcs as depicted in Figure 7. The decrease in capacitance with increasing frequency was due to the slow release of charge carriers from relatively deep traps [25], capacitance attain the constant value at higher frequency and was strongly frequency dependent relatively at low frequencies. The trend in plot of capacitance variation with frequency may be attributed to the blocking of charge carriers at the electrodes. Effectively the charge carriers present in the pellet migrate when a field is applied, and due to the impedance to their motion at electrodes, there was a large increase in the capacitance at low frequencies. Similar behavior has been reported by on semiconducting phthalocyanines [26].

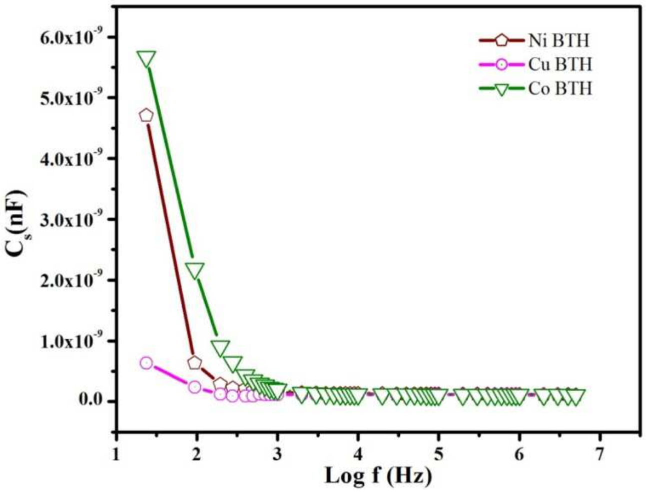


Figure: 7 shows Variation in the capacitance with log of frequency for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines at room temperature

Dielectric loss (tan δ) Properties as a function of frequency

The loss tangent factor decreases with increase of frequency as displayed in Figure 8. The variation of tan δ with log (frequency) was virtually constant after 3.6 KHz higher frequency at room temperatures and the shoulder plots not perceived in the measured frequency range, it may lie beyond the frequency range of measured and this due to the effect of face resistances [27], in context electrical conduction losses increase which increases the value of the dielectric loss [28].

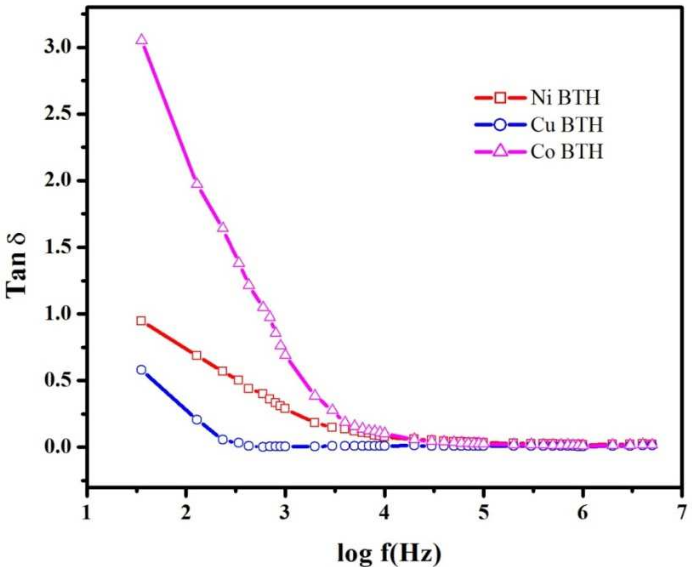


Figure: 8 shows the frequency dependence of the Dielectric loss with log of frequency for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines at room temperature

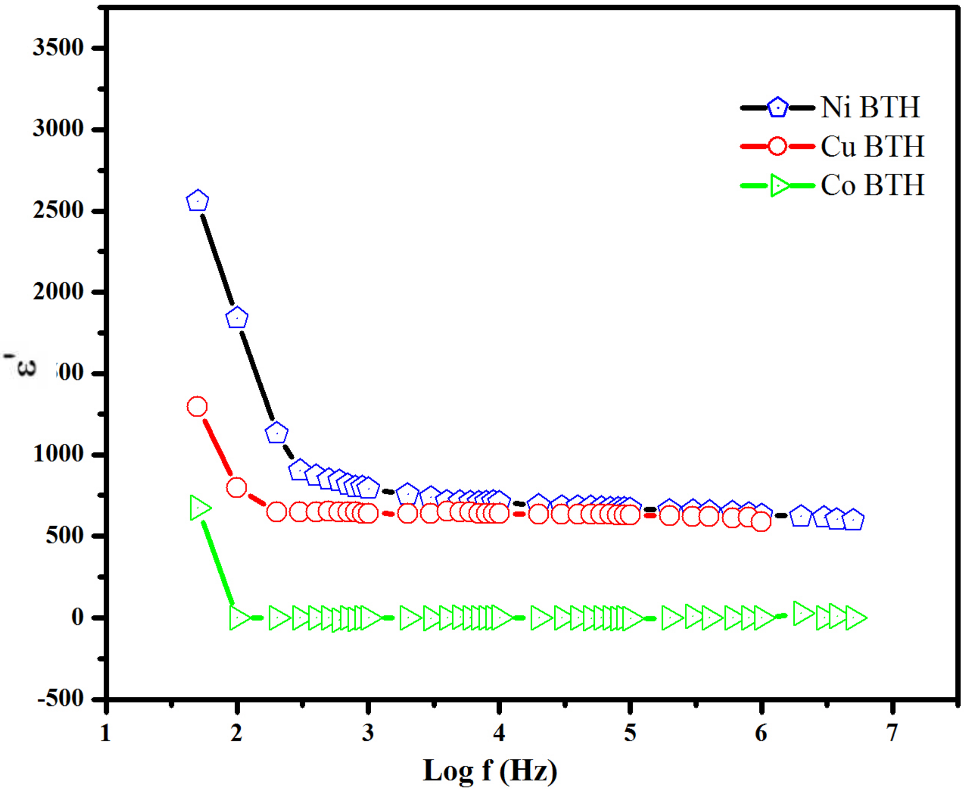


Figure: 9 show the frequency dependence of the Dielectric constant with log of frequency for 3-chlorobenzothiophene-1,3,4-oxadiazole substituted metallophthalocyanines at room temperature

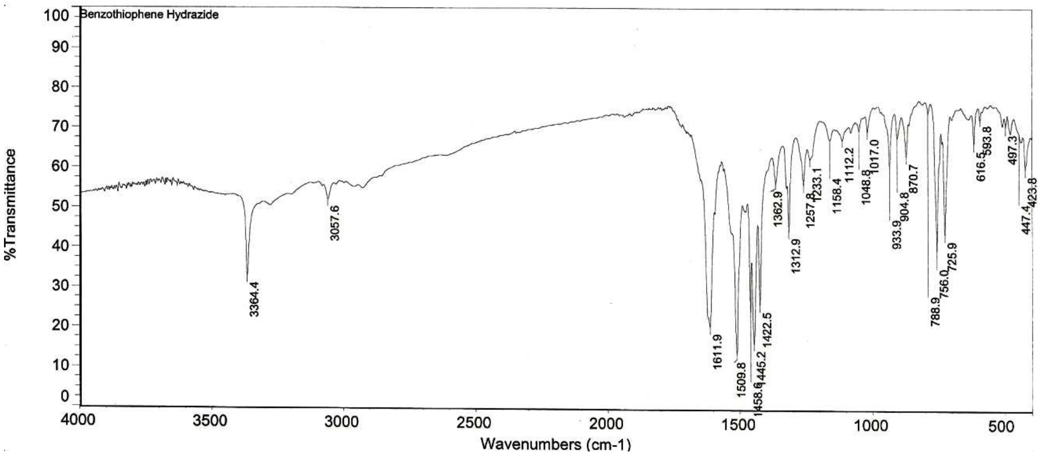
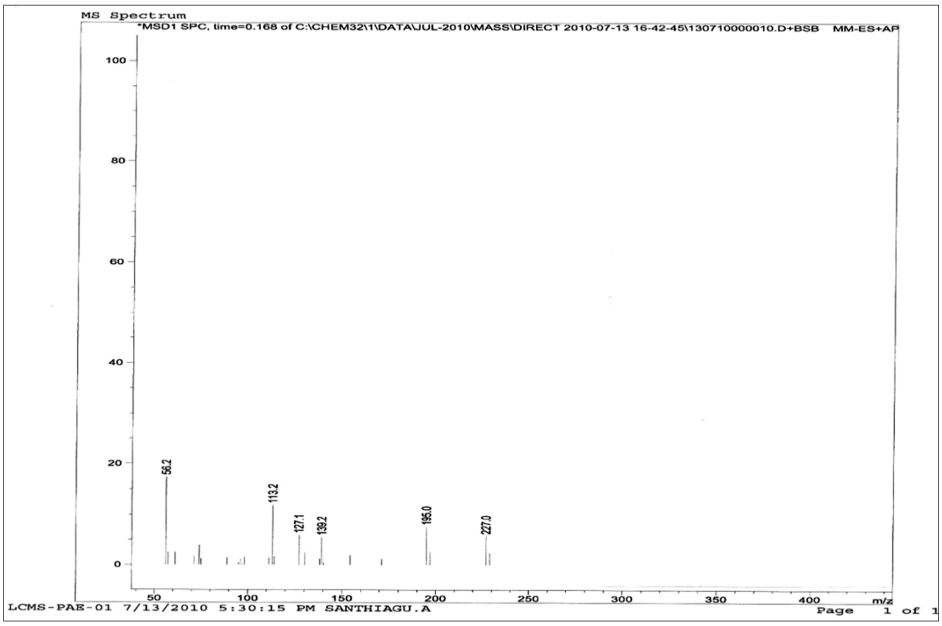


Figure: 10 IR spectra for 3- chlorobenzothiophene hydrazide.



Dielectric Constant Properties as a function of frequency:

The changes in comparative permittivity (dielectric constant) with frequency are revealed in Figure 9. From the graph its clearly revealed that dielectric constant decreases with increasing frequency it can be seen that ε' monotonically with increasing frequency and attains a constant value at higher frequencies, due to the dielectric dispersion resulting from the lag of molecular polarization behind the alternations of the applied electric field. Low value of dielectric constant at higher frequencies may be due to the loss of significance of space charge polarization gradually [29, 30]. The increase of the dielectric constant with decrease in frequency can be attributed to the presence of dipoles. This result suggests a major improvement over what has been reported in the past with Pc related materials. The dielectric constant ranges between 500 and 2600 Hz with respective frequency, which was quite high compared with the conventional unsubstituted phthalocyanine and dielectric constant was due to nomadic polarization as envisaged by Norrell et al [31] and Pohl [32,]. Possibly, the delocalization within the phthalocyanines macrocycles permits easy displacement of the n-electrons over the microcrystalline regions, leading to polarizability and enhanced dielectric constant. Phthalocyanines are aromatic molecules having a highly conjugated structure, thus nomadic polarization can arise due to the presence of appreciable numbers of free charges and long domains. This result indicates that there are remarkable changes within the dielectric parameters due to the peripheral substitution since the π-electron system has been enhanced by the phthalocyanines and showing possible application in the field of sensors, actuators, artificial muscles, as well as bypass capacitors in microelectronics and energy-storage devices.

CONCLUSION

We successfully appended the electron-deficient 3-chlorobenzothiophene onto electron-rich phthalocyanines via 1,3,4-oxadiazole bridge to improve the thermal stability. UV absorption studies shows hard splitting of Q band in the region 600. From X-ray diffraction analysis it is clear that the structure of phthalocyanines molecule are amorphous and results shows that large conjugated system exists in molecule. Ac conductivity was measured as function of frequency at room temperature and shows a strong frequency dependence in the investigated frequency range at room temperature, conductivity studies are qualitatively in excellent conformity with the results of 3-chlorobenzothiophene l-(1,3,4)-oxadiazole substituted MPcs compounds.The results reported here serve to demonstrate to construct new type phthalocyanines complexes combining the features and properties of phthalocyanines in wider temperature applications with high frequency devices could be advantageous.

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Authors' contributions
We were synthesized new type of substituted metallophthalocyanines which contain hetero atom with highly conjugated and produced the spectral data presented molecule. All authors read and approved the final manuscript.

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