5-amino-[1,3,4]-oxadiazole and 5-amino-[1,3,4]-thiadiazole appended metal phthalocyanines: Synthesis, Optical and Electrical studies
2.1. Introduction

Phthalocyanines (Pcs) and related macrocyclic systems have engrossed significant interest for many decades because of their diverse applications, such as photocopiers and printers [1], photovoltaic cells [2], gas sensors [3], nonlinear optical limiting devices [4] and photodynamic therapy agents [5–9] and catalysis [10]. These versatile features have stimulated the synthesis of phthalocyanine (Pc) derivatives with new structural and functional subunits.

Variety of aromatic heterocycles like oxadiazole, thiadiazoles, triazoles, pyridine and quinoline based moieties have been suggested as good electron transport and hole blocking materials for electroluminescent devices [11–14]. Recently, many peripherally heterocyclic moieties substituted Pc derivatives have been reported with attractive physicochemical properties and electrical properties [15–19]. Our recent contributions describing a series of Pes with aryl and alkyl-[1,3,4]-oxadiazole subunits which exhibited admirable optical, thermal and electrical properties [20, 21]. These results encouraged us to explore properties of different transition metal phthalocyanines (MPc) appended with heterocyclic subunits such as 5-amino-[1,3,4]-oxadiazole and 5-amino-[1,3,4]-thiadiazole entities (MPc1-6) was synthesized (Scheme-1).

Understanding the electronic charge transport processes in Pcs is interesting both from fundamental and technological point of view. In recent years, owing to their very interesting physical properties, this particular family of materials has raised considerable deal of research interest followed by technological applications in the field of micro/optoelectronics [22–24]. Semiconducting behaviour of phthalocyanine is p-type at all temperature [25]. An important aspect for the study of the dielectric properties of materials is to understand certain physical properties of the system, like
the presence of impurities, voids, structural defects, various polarization and relaxation mechanics etc. [26]. The Chapter deals with the frequency dependence of AC conductivity, dielectric constant and dielectric loss studies have been performed for MPe1-6 in bulk form. The measurements have been carried out in the frequency range of 50 Hz to 5 MHz at room temperature.

2.2. Experimental

2.2.1. Materials

1,2,4-Benzene tricarboxylic anhydride (trimellitic anhydride) was purchased from Sigma Aldrich. Semicarbazide and thiosemicarbazide were purchased from Merck (India) and used without purification. Other reagents were purchased from Himedia Chemicals Ltd. India.

2.2.2. Instrumentation

Elemental analysis was obtained from a Carlo-Erba 1106 instrument. Infrared (IR) spectra were recorded on a FT-IR 8400s Shimadzu spectrometer in KBr pellets. Solid state electronic absorption spectra were recorded on a UV-Vis NIR spectrometer, model USD 4000. Solid-state $^{13}$C-NMR spectra were recorded on a Bruker DSX-300 solid-state NMR spectrometer with a magnetic field of 7.04T and carbon frequency of 75.47 MHz (internal standard was glycine). Perkin-Elmer Thermal analyzer is used for TGA. Powdered XRD measurements were carried out on a Bruker D8 Advance X-ray diffractometer. The dielectric and ac conductivity measurements were carried out using impedance analyzer model HIOKI 3352-50 HiTESTER Version 2.3.
2.2.3. General method for the synthesis of tetracarboxy metal phthalocyanines (TCMPC (M=Co, Ni & Cu)) [Scheme1].

The mixture of trimellitic anhydride (10g, 0.05 mol), urea (30g, 0.5 mol), ammonium chloride (1.25g, 0.023 mol), ammonium molybdate (1g, 0.8 mmol) and the required metal salt (0.06 mol): {i.e. cobalt (II) chloride for cobalt tetra carboxylic acid phthalocyanine (CoTCPc), nickel (II) chloride for nickel tetra carboxylic acid phthalocyanine (NiTCPc) and copper (II) chloride for copper tetra carboxylic acid phthalocyanine (CuTCPc)} were finely ground and added to nitrobenzene (150 ml). The mixture was stirred by using mechanical stirrer for 6 hours at 180–190 °C. A dark-blue solid resulted which was filtered off and washed with methanol under Soxhlet extraction until the smell of nitrobenzene could no longer be detected. Potassium hydroxide (10%, enough to dissolve the resulting solid) was added to the solid mixture and stirred for 12 h at 80–90 °C, allowed to cool to room temperature and the insoluble impurities separated by centrifugation. The resulting fluid was acidified with concentrated hydrochloric acid (HCl) to precipitate the carboxylic acid metal phthalocyanines, which was filtered, washed three times with water and then with dilute HCl followed by water and methanol until the filtrate to be colourless, dried in oven at 60 °C for 24 h [27].

2.2.3.1. Tetra carboxy cobalt phthalocyanine (CoTCPc).

Yield (77%), Calcd: C (57.86), H (2.16), N (15.00), O (17.13). Found: C (57.25), H (2.01), N (15.44), O (17.02). IR [(KBr) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3359 (\(-\text{OH}\)), 2945 (Ar-CH), 1609 (C=O), 1496 (C=N), 1320, 1138, 1094, 923, 836, 726, 431. UV-Vis (solid state) \(\lambda_{\text{max}}/\text{nm}\): 337, 433, 547.
2.2.3.2. Tetra carboxy nickel phthalocyanine (NiTCPc).

Yield (80%), Calcd: C (57.86), H (2.16), N (14.99), O (17.12). Found: C (57.19), H (2.02), N (15.21), O (16.98). IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3365 (-OH), 2939 (Ar-CH), 1613 (C=O), 1506 (C=N), 1321, 1141, 1088, 926, 838, 727, 470. UV-Vis (solid state) $\lambda_{\text{max}}/\text{nm}$: 337, 438, 555. $^1$H NMR (DMSO/TMS) $\delta$ ppm: 6.5–8.32 (12H Ar-H) & 12.3 (4H -COOH). $^{13}$CNMR (Solid State) $\delta$ ppm 195,164, 127.

2.2.3.3. Tetra carboxy copper phthalocyanine (CuTCPc).

Yield (82%), Calcd: C (57.86), H (2.16), N (14.99), O (17.12). Found: C (57.22), H (2.03), N (15.27), O (16.96). IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3361 (-OH), 2933 (Ar-CH), 1614 (C=O), 1504 (C=N), 1370, 1143, 1094, 914, 843, 733, 433. UV-Vis (solid state) $\lambda_{\text{max}}/\text{nm}$: 337, 442, 566.

2.2.4. General method for the synthesis of tetra-5-amino-[1,3,4]-oxadiazole and tetra-5-amino-[1,3,4]-thiadiazole substituted MPcs (M=Co, Ni & Cu) (1-6) [Scheme 2].

Tetra-5-amino-[1,3,4]-oxadiazole and tetra-5-amino-[1,3,4]-thiadiazole substituted MPC1-6 were synthesized by adopting the procedure earlier reported by us [20, 21]. In brief TCMPc (0.001 mol) and semicarbazide (0.006 mol) or thiosemicarbazide (0.006 mol) were stirred in preheated 100g polyphosphoric acid (PPA) containing 10g P$_2$O$_5$ and the reaction mixture was maintained at 150 °C for 20 h. The product obtained was repeatedly treated with 0.1 N sodium hydroxide solution followed by water and acetone to get pure tetra-5-amino-[1,3,4]-oxadiazole and tetra-5-amino-[1,3,4]-thiadiazole substituted MPC1-6.

2.2.4.1. Tetra-[5-(amino)[1,3,4]-oxadiazole]-cobalt phthalocyanine (MPC1).

Yield: 90%. Calcd: C (56.87), H (2.39), N (33.16), O (7.58). Found: C (56.25), H
(2.11), N (33.04), O (7.18). IR [(KBr) $\nu_{\text{max}}$/cm$^{-1}$]: 2924 (Ar-CH), 3170 (-N-H), 1609 (C=N), 1496 (C=C), 1150 (-C-O), 1094, 923, 823, 728 (Pc skeleton vibration). UV-Vis (solid state) $\lambda_{\text{max}}$/nm 434, 580, 793.

2.2.4.2. Tetra-{5-(amino)[1,3,4]-oxadiazole}-nickel phthalocyanine (MPc2).

Yield: 84%. Calcd: C (56.87), H (2.39), N (33.16), O (7.58). Found: C (56.23), H (2.12), N (32.94), O (7.28). IR [(KBr) $\nu_{\text{max}}$/cm$^{-1}$]: 2919 (Ar-CH), 3164 (-N-H), 1613 (C=N), 1525 (C=C), 1141 (-C-O), 1088, 926, 838, 727 (Pc skeleton vibration). $^{13}$C-NMR (solid state)$\delta$ ppm; 165, 144,134-122. UV-Vis (solid state) $\lambda_{\text{max}}$/nm; 434, 591, 843.

2.2.4.3. Tetra-{5-(amino)[1,3,4]-oxadiazole}-copper phthalocyanine (MPc3).

Yield: 93%. Calcd: C (56.87), H (2.39), N (33.16), O (7.58). Found: C (56.29), H (2.17), N (32.99), O (7.32). IR [(KBr) $\nu_{\text{max}}$/cm$^{-1}$]: 2923 (Ar-CH), 3173 (-N-H), 1614 (C=N), 1504 (C=C), 1143 (-C-O), 1094, 914, 843, 733 (Pc skeleton vibration). UV-Vis (solid state) $\lambda_{\text{max}}$/nm; 431, 584, 780.

2.2.4.4. Tetra-{5-(amino)[1,3,4]-thiadiazole}-cobalt phthalocyanine (MPc4).

Yield: 87%. Calcd: C (52.85), H (2.22), N (30.82), S (14.11). Found: C (52.26), H (2.00), N (30.43), S (13.81). IR [(KBr) $\nu_{\text{max}}$/cm$^{-1}$]: 2923 (Ar-CH), 3172 (-N-H), 1609 (C=N), 1496 (C=C), 728 (-C-S), 1094, 923, 836, 728 (Pc skeleton vibration). UV-Vis (solid state) $\lambda_{\text{max}}$/nm; 434, 576, 809.

2.2.4.5. Tetra-{5-(amino)[1,3,4]-thiadiazole}-nickel phthalocyanine (MPc5).

Yield: 90%. Calcd: C (52.85), H (2.22), N (30.82), S (14.11). Found: C (52.28), H (2.02), N (30.51), S (13.89). IR [(KBr) $\nu_{\text{max}}$/cm$^{-1}$]: 2918 (Ar-CH), 3143 (-N-H), 1611...
2.2.4.6. Tetra-{5-(amino)[1,3,4]-thiadiazole}-copper phthalocyanine (MPC6).

Yield: 85%. Calcd: C (52.85), H (2.22), N (30.82), S (14.11). Found: C (52.36), H (2.03), N (30.45), S (13.92). IR [(KBr) ν max/cm⁻¹]: 2922 (Ar-CH), 3173 (-N-H), 1613 (C=N), 1503 (C=C), 733 (-C-S), 1093, 913, 840, 733 (Pc skeleton vibration). UV-Vis (solid state) λ max/nm: 434, 597, 847.

2.2.5. Electrical measurements

Devices were fabricated in a sandwich configuration Ag/MPC/Ag with powdered MPC(4-6) samples were 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 conductivity measurements were carried out using impedance analyzer model HIOKI 3352-50 HiTESTER Version 2.3. The measurements were carried out at room temperature in between the 50Hz–5MHz. The capacitance value (C), and AC conductance (G) were directly obtained from the instrument. The dielectric constant (ε') and AC conductivity (σ_ac) values are calculated using the relations ε' = ε₀d/ε_acA and σ_ac = Gd/A respectively. Where, ‘d’ is the thickness of the sample and ‘A’ is the cross-section area and ε₀ is the permittivity of the free space.

2.3. Results and Discussion

2.3.1. Synthesis

Tetra carboxy metal phthalocyanines are synthesized from trimellitic anhydride by cyclotetramerization reaction [27] and the spectral data confirms the synthesized...
starting materials as desired. Melt condensation of tetracarboxy transition metal phthalocyanines with semicarbazide or thiosemicarbazide resulted in the formation of 2,9,16,23-tetra-5-amino-[1,3,4]-oxadiazole and 2,9,16,23-tetra-amino-[1,3,4]-thiadiazole-substituted metal phthalocyanines (MPc1-6) (M = Co, Ni and Cu). The condensation was realized in the presence of PPA at 150-160 °C. And all the new Pc complexes were characterized by elemental analysis, FT-IR, solid-state UV-Vis, solid-state $^{13}$C-NMR spectroscopy, thermal analyses and XRD studies.

Scheme 1. Synthesis of tetra carboxy metal phthalocyanines (TCMP, M= Co, Ni & Cu).

Scheme 2. Synthesis of tetra amino-[1,3,4]- oxadiazole and tetra amino-[1,3,4]-thiadiazole-substituted MPcs1-6 (M= Co, Ni and Cu) complexes.
2.3.2. FT-IR Spectra

FT-IR spectra of complexes \textbf{MPCl-6} show in figures 1 and 2, exhibited a series of absorptions at 727–733, 823–843, 913–926 and 1088–1094 cm\(^{-1}\) which can be attributed to the Pc skeleton. Peaks at 1609–1614 and 1496–1525 cm\(^{-1}\) for MPCl-6 are assigned to aromatic \(-\text{C=}=\text{N}-\) and \(-\text{C}=\text{C}-\) in plane skeletal vibrations of the Pc core. Peaks at 2918–2924 cm\(^{-1}\) and 1088–1094 cm\(^{-1}\) are associated with aromatic \(-\text{C}–\text{H}\) stretching and aromatic \(-\text{C}–\text{H}\) bending vibrations respectively. The \(-\text{N}–\text{H}\) stretching vibrations of primary \(-\text{NH}_2\) attached to oxadiazole and thiahdiazole rings appeared at 3143–3173 cm\(^{-1}\). Comparison of FT-IR spectra of basic TCMPc and ensuing MPCl-6 reveals some marked differences; the characteristic intense absorption due to \(-\text{C}–\text{O}\) (\(-\text{COOH}\)) of TCMPc (\(\text{M} = \text{Co, Ni \& Cu}\)) at \(\sim 1700\) cm\(^{-1}\) disappear in the IR spectra of MPCl-6 indicating involvement of carboxyl group in condensation followed by cyclization with semicarbazide and thiosemicarbazide. The characteristic stretching vibrations due to \(-\text{C}=\text{N}-\), \(-\text{C}–\text{O}\) and \(-\text{C}–\text{S}\) for oxadiazole and thiahdiazole rings are found to be coupled with skeletal vibrational peaks of \(-\text{C}=\text{N}-\), \(-\text{C}=\text{C}-\) and of the Pc core.

![Figure 1](image.png)

\textbf{Figure 1.} IR-spectra of NiTCP and for MPCl-3 complexes.
2.3.3. **Solid-state $^{13}$C-NMR spectra**

The NiTCPc is a well studied molecule, its $^1$H-NMR and Solid state $^{13}$C-NMR spectral data clearly confirms its formation. Solid-state $^{13}$C-NMR spectra of complexes MPc2 and 5 are presents in figures 3 and 4. The MPc complexes 2 and 5 exhibits the expected broad signal at 122-134 ppm and an additional peak at 142-144 ppm for aromatic carbons and aromatic carbons attached to oxadiazole, thiadiazole and nitrogen, respectively. Peaks at 172-165 ppm were assigned to carbons of oxadiazole...
and thiadiazole subunits. Unfortunately, NMR spectroscopy is uninformative in case of cobalt and copper metal centres, because the paramagnetic character prevents the resolution of the signals [28].

![Figure 4. Solid-state C\(^{13}\) spectra of NiPc5.](image)

2.3.4. Electronic absorption spectra

Electronic absorption spectra are fruitful to establish the structure of phthalocyanines. Solid-state electronic absorption spectra of compounds MPc1–6 are presented in figures 5 and 6. Phthalocyanines demonstrate strong absorption in two distinct edges of visible region, namely Q-band and Soret-band (B bands). The location of the Soret bands (B bands) is quite similar for all MPc1–6 in range 431–434 nm and the characteristic Q-band appeared in the range 576–597 nm with marginal splitting along with an additional band of considerable intensity in near-IR region at \( \approx 800 \) nm. The presence of heteroaromatic ring systems (oxygen, nitrogen and sulfur) in the MPc1–6 periphery lead to immense extension of \( \pi \)-conjugation inducing red shift and splitting of the Q-band, which may be attributed to \( a_{2u}^{-1}c_{g} \) and \( b_{2u}^{-1}c_{g} \) transitions [29, 30] indicating effective electronic communiqué between the two different ring systems with Pc core [31]. Further the peak broadening is due to aggregation of Pc molecules owing to extended conjugation [32, 33].
Optical band gaps of complexes MPc1–6 were determined by the absorption lower edge of the absorption spectrum of each compound in the solid state and the data are summarized in table 1. Since interactions of MPc molecules are of van-der-waals type and the presence of heteroaromatic ring systems in the MPc periphery results in rearrangements of molecule and alter the energy band gap between valence and conduction bands.

![Absorption Spectra](image1)

**Figure 5.** Solid-state electronic absorption spectra of MPc1–3 complexes.

![Absorption Spectra](image2)

**Figure 6.** Solid-state electronic absorption spectra of MPc4–6 complexes.
Table 1. Optical band gap data of MPc1-6.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peaks $\lambda_{\text{max}}$(nm)</th>
<th>Band gap(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPc1</td>
<td>434 580 793</td>
<td>2.23 1.75 1.32</td>
</tr>
<tr>
<td>MPc2</td>
<td>434 591 843</td>
<td>2.20 1.69 1.07</td>
</tr>
<tr>
<td>MPc3</td>
<td>431 584 780</td>
<td>2.51 1.72 1.39</td>
</tr>
<tr>
<td>MPc4</td>
<td>434 576 809</td>
<td>2.24 1.74 1.27</td>
</tr>
<tr>
<td>MPc5</td>
<td>434 597 847</td>
<td>2.32 1.56 1.08</td>
</tr>
<tr>
<td>MPc6</td>
<td>434 578 804</td>
<td>2.32 1.77 1.37</td>
</tr>
</tbody>
</table>

2.3.5. Thermal Analysis

Thermo gravimetric investigation of MPc1-6 complexes show in figures 7 and 8 indicates that the complexes undergo decomposition in three steps. The first step of the degradation in the temperature region around 110 °C may be accounted for the loss of moisture. The second degradation step in the temperature range 355-480 °C for MPc1-3 and 400-510 °C for MPc4-6 can be accounted for the loss of peripheral substitution. The third step of gradual decomposition observed in the temperature range 410-530 °C for MPc1-3 and 475-590 °C for MPc4-6 are attributed for phthalocyanine core. The thermal analysis gives the stability of MPc1-6 complexes, all shows stability $>350$ °C.

Kinetic and thermodynamic parameters were computed using Broido’s method [34]. Plots of $-\ln(\ln(1/\text{Y}))$ versus $1/T$ (figures 9 and 10) (where Y is the fraction of the compound undecomposed) were developed for the decomposition segment. From the
plots, the activation energy (Ea) and frequency factor (lnA) were evaluated. The enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been computed using standard equations and are summarized in Table 2.

![Figure 7](image_url)  
**Figure 7.** TGA graphs of MPc1–3 complexes.

![Figure 8](image_url)  
**Figure 8.** TGA graphs of MPc4–6 complexes.
Figure 9. Plots of $-\ln(\ln(-1/y))$ vs $1/T \times 10^3$ for the second step decomposition of oxadiazole and thiadiazole moieties in MPc1–6.

Figure 10. Plots of $-\ln(\ln(-1/y))$ vs $1/T \times 10^3$ for the third step decomposition of Pc skeleton in MPc1–6.

2.3.6. XRD studies

The powdered XRD patterns of MPc1-6 are presented in figure 11. The diffraction pattern exhibited characteristic broad peaks. The heteroaromatic oxadiazole and thiadiazole rings in the Pc periphery result in extended conjugation and the greater $\pi$-electron region influences the stacking of the Pcs in parallel molecules and the ensuing compounds were amorphous in nature.
Table 2. Kinetic and thermodynamic parameters of MPc1–6 complexes.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Decomposition Range (°C)</th>
<th>Ea (kJ/mol)</th>
<th>lnA</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (kJ/K)</th>
<th>ΔG (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPc1</td>
<td>395-480</td>
<td>0.007271</td>
<td>-7.8691</td>
<td>-5.89567</td>
<td>-160.520</td>
<td>113.96</td>
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<tr>
<td></td>
<td>480-530</td>
<td>0.098623</td>
<td>3.7762</td>
<td>-6.36967</td>
<td>-143.788</td>
<td>111.86</td>
</tr>
<tr>
<td>MPc2</td>
<td>355-410</td>
<td>0.012173</td>
<td>-7.0228</td>
<td>-5.43315</td>
<td>-161.170</td>
<td>105.56</td>
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<tr>
<td></td>
<td>410-485</td>
<td>0.030844</td>
<td>-4.2586</td>
<td>-5.95524</td>
<td>-157.162</td>
<td>113.15</td>
</tr>
<tr>
<td>MPc3</td>
<td>375-445</td>
<td>0.019972</td>
<td>-5.7859</td>
<td>-5.65849</td>
<td>-159.314</td>
<td>108.80</td>
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<tr>
<td></td>
<td>445-500</td>
<td>0.016904</td>
<td>3.1630</td>
<td>-5.69703</td>
<td>-157.274</td>
<td>112.46</td>
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<tr>
<td>MPc4</td>
<td>435-510</td>
<td>0.017551</td>
<td>-6.0073</td>
<td>-6.17638</td>
<td>-159.469</td>
<td>118.79</td>
</tr>
<tr>
<td></td>
<td>510-590</td>
<td>0.087766</td>
<td>3.1989</td>
<td>-6.75466</td>
<td>-138.618</td>
<td>114.07</td>
</tr>
<tr>
<td>MPc5</td>
<td>440-510</td>
<td>0.042999</td>
<td>-2.7484</td>
<td>-6.17587</td>
<td>-157.518</td>
<td>117.81</td>
</tr>
<tr>
<td></td>
<td>510-570</td>
<td>0.111466</td>
<td>5.7981</td>
<td>-6.64782</td>
<td>-127.541</td>
<td>103.68</td>
</tr>
<tr>
<td>MPc6</td>
<td>400-475</td>
<td>0.015364</td>
<td>-6.4216</td>
<td>-5.88758</td>
<td>-160.305</td>
<td>113.81</td>
</tr>
<tr>
<td></td>
<td>475-525</td>
<td>0.131760</td>
<td>6.8438</td>
<td>-6.29496</td>
<td>-154.369</td>
<td>119.32</td>
</tr>
</tbody>
</table>

Figure 11. XRD graphs of MPc1–6 complexes.
2.3.7. **AC electrical measurements**

2.3.7.1. **Frequency dependence of Dielectric constant ($\varepsilon'$)**

Figure 12 and 13 shows variation of $\varepsilon'$ with frequency for the complexes MPc1-6 at room temperature. Initially, $\varepsilon'$ decreases with increase in frequency and finally at higher frequencies reaching a constant value for all the complexes MPc1-6. The researcher reported $\varepsilon'$ value ~20000 at 120 °C for phthalocyanine [35], but the complex MPc3 shows high $\varepsilon'$ value 22500 at room temperature. The high dielectric constant materials are useful for the fabrication of many electronic devices such as capacitors and for a variety of artifacts, such as rectifiers and semiconductor devices, piezoelectric transducers, dielectric amplifiers, and memory elements [36]. The observed large values of $\varepsilon'$ at lower frequencies are attributed to the charge carriers present in the material (MPc), which migrate upon the application of the field. The decrease in $\varepsilon'$ may be due to the decrease in space charge carries or interfacial polarization in the Pc material [37, 38]. That is at low frequencies; the dipoles align themselves along the field and contribute fully to the total polarization.

![Figure 12. Variation of dielectric constant with frequency of MPc1–3 complexes.](image-url)
At higher frequency's, variation in the field is too rapid for the dipoles to align themselves. So $\varepsilon'$ variation is small, becomes nearly frequency independent and approaches a constant value as can be seen clearly in figure 12 and 13. This can be attributed to rapid polarization process [39].

2.3.7.2. Frequency dependence of dielectric loss (tan$\delta$)

The figure 9 and 10 shows the variation of dielectric loss tangent (tan$\delta$) with frequency for the complexes MPc1-6 at room temperature. It is observed from the figure 14 and 15 that the tan$\delta$ decreases with increasing frequency with shoulder nature for MPc1, MPc3 and MPc4. The observation of shoulder in the MPc1, MPc3 and MPc4 indicates the presence of resonance between the hooping frequency of the charge carriers and applied frequency. For complexes MPc2, MPc5 and MPc6 the shoulder behaviour is not observed in the measured frequency range. This may be due to the resonance frequency for the complexes MPc2, MPc5 and MPc6 lie behind the frequency range of measurement [40].

Figure 13. Variation of dielectric constant with frequency of MPc4–6 complexes.
2.3.7.3. Frequency dependence of AC conductivity ($\sigma_{ac}$)

The AC conductivity ($\sigma_{ac}$) has been measured for bulk metalphthalocyanine in the form of compressed pellet Ag/MPc/Ag (M= Co, Ni and Cu) in the frequency range of 50Hz to 5MHz utilizing an oscillating voltage with amplitude 1V peak-to-peak.
Results have been reported for pellets of MPc1-6 maintained under vacuum. Figure 16 and 17 displays the frequency dependence of AC conductivity for MPc1-6 complexes at room temperature revealing an increasing trend in the conductivity with the change of frequency, which is due to an increased density of charge carriers for conduction. In particular, the AC conductivity of the complexes MPc2, MPc4, MPc5 and MPc6 is found to remain constant for increase in the frequency from 50Hz to 1MHz and found to increase suddenly for further increase in the frequency up to 5MHz [41], whereas for the complexes MPc1 and MPc3, the ac conductivity is found to increase with the increase in frequency from 50Hz to 5MHz. The observed trends in frequency dependence of ac conductivity can be explained on the basis of electron hooping model. In general, decrease in conductivity with increasing frequency is associated with a band-type conduction process and increase in the conductivity with a frequency is a hopping-type conduction mechanism [42] and complexes MPc1 and MPc3 shows better conductivity.

![Figure 16](image)

**Figure 16.** Variation of AC conductivity with frequency of MPc1–3 complexes.
Conclusion

The ensuing MPc1-6 complexes with the existence of oxadiazole and thiadiazole moieties resulted in admirable thermal stability (>350 °C) & exhibited maximum visible window absorption from 400 to 800 nm and very large red shift effects of Q band with decreased optical band gap of MPc1-6. The dielectric constant ($\varepsilon'$) values were found to decrease with an increase in the frequency. The complex MPc3 at 50 Hz frequency shows high $\varepsilon'$ value 22500 at room temperature. The high $\varepsilon'$ materials are useful for the fabrication of many electronic devices such as capacitors & for a variety of artifacts, such as rectifiers and semiconductor devices and memory elements. The dielectric loss tangent (tanδ) values were also found to decrease with an increase in the frequency. However, shoulder nature is observed in the variation of tanδ with frequency for MPc1, MPc3 and MPc4, which is understood on the basis of resonance between hopping frequencies of charge carriers and applied frequency. The AC conductivity for the MPc1-6 complexes is found to increase with an increase in the frequency. The electrical conduction mechanism of MPc1-6 is found to be in accordance with the electron hopping model.
References


