Effect of substitution group on dielectric properties of 4H-pyrano [3, 2-c] quinoline derivatives thin films

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The AC electrical conductivity and dielectrical properties of 2-amino-6-ethyl-5-oxo-4-(3-phenoxyphenyl)-5,6-dihydro-4H-pyrano[3, 2-c]quinoline-3-carbonitrile (Ph-HPQ) and 2-amino-4-(2-chlorophenyl)-6-ethyl-5-oxo-5,6-dihydro-4H-pyrano [3, 2-c] quinoline-3-carbonitrile (Ch-HPQ) thin films were determined in the frequency range of 0.5 kHz–5 MHz and the temperature range of 290–443 K. The AC electrical conduction of both compounds in thin film form is governed by the correlated barrier hopping (CBH) mechanism. Some parameters such as the barrier height, the maximum barrier height, the density of charges, and the hopping distance were determined as functions of temperature and frequency. The phenoxyphenyl group has a greater influence on those parameters than the chlorophenyl group. The AC activation energies were determined at different frequencies and temperatures. The dielectric behaviors of Ph-HPQ and Ch-HPQ were investigated using the impedance spectroscopy technique. The impedance data are presented in Nyquist diagrams for different temperatures. The Ch-HPQ films have higher impedance than the Ph-HPQ films. The real dielectric constant and dielectric loss show a remarkable dependence on the frequency and temperature. The Ph-HPQ has higher dielectric constants than the Ch-HPQ.

Keywords: thin films, quinoline derivatives, dielectrical properties, correlated barrier hopping

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1. Introduction

In recent years, organic thin films have played an important role in device fabrication. Thin films of quinoline derivatives deposited on a solid state substrate are one example of such films. Quinoline is a heterocyclic organic compound in which one or more of the ring carbon atoms are replaced by another element such as nitrogen, oxygen, and sulfur.[1] Quinoline and its derivatives are π-conjugated semiconductor materials with a unique combination of high thermal stability, easy processing, and high photoluminescence (PL) quantum yield.[2] Quinoline derivatives offer the promise of wide spread adoption in numerous areas of technology including the organic light emitting diode (OLED),[3] information storage,[4] non-linear optical material,[4] and optoelectronic devices.[5] Many polyquinolines were developed and their optical and spectroscopic properties were investigated.[6]

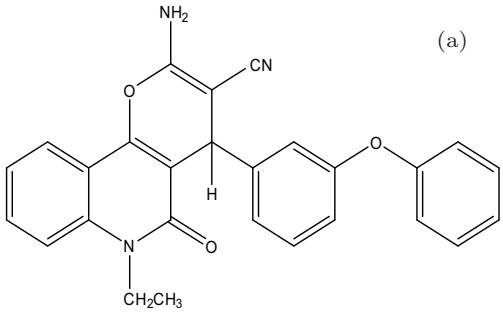
It is well known that the substitution atoms or groups affect the chemical and physical properties of the organic compounds. The structural, thermal, optical, photovoltaic, electrical, and dielectrical properties of the compounds depend on the type of the substitution atoms or function groups. In the conjugated organic compounds, such as phthalocyanine and porphyrins, their electrical and dielectrical properties are improved by inserting a metal at the center of the ring or by attaching a substitution group to it.[7–14] The presence of different substitution groups on the quinoline ring (i.e., electron withdrawing group, electron donating group, and metal complex) has a great influence on its structural and physical properties. El-Ghamaz *et al.*[15] have reported on the azo dye heterocyclic complexes of Cu (II), Co (II), and Ni (II). It was found that the type of the metal affects the thermal and dielectrical properties. The presence of NO_2, as a strong electron withdrawing group in the azo quinoline, increases the AC electrical conductivity and the dielectric constants.[16] The AC conductivity and dielectrical properties of ligands (5-(4'-derivatives phenylazo)-2 thioxothiazolidin-4-one) and their complexes have been investigated.[17,18] The electrical conductivity was found to be dependent on the structure of the substitution group. It was found that the change of the substituent for complexes affects the type of conduction mechanism.[17]

The AC conductivity measurements can be used to characterize the electrical properties of various materials. These measurements provide deep understanding of the nature of the conduction mechanism, and they also provide information about the interior of the materials in the region of relatively low conductivity.[19] Also, these measurements help in distinguishing between localized and free band conductions. In case of localized conduction, the AC conductivity increases with frequency, while in the free band conduction, the conductivity decreases with frequency.[20]

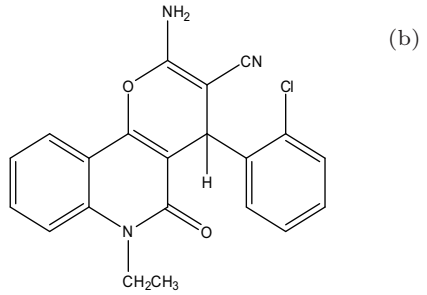
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Therefore, in this paper, an extensive investigation comparing the effects of two different donor substitution groups, namely, chlorophenyl and phenoxyphenyl, on the electrical and dielectrical properties of 4H-pyrano [3, 2-c] quinoline (HPQ) thin films is performed. For the chlorophenyl case, the carbon–chlorine bond is enriched with an electron by an inductive effect.[21] So the chlorophenyl is a donor substitution group with respect to the HPQ compound. In the phenoxyphenyl case, the oxygen as a substitution atom has a lone pair of electrons that are shared with the aromatic ring. So the phenoxyphenyl is also a donor substitution group with respect to the HPQ compound, and phenoxyphenyl is a stronger donor substitution group than chlorophenyl.



2-amino-6-ethyl-5-oxo-4-(3-phenoxyphenyl)-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile



2-amino-4(2-chlorophenyl)-6-ethyl-5-oxo-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile

Fig. 1. Molecular structures of (a) Ph-HPQ and (b) Ch-HPQ compounds.

2. Experimental details

2.1. Preparation of thin films

Ph-HPQ and Ch-HPQ in powder form were synthesized in accordance with the methods reported earlier in Ref. [22]. Thin films, with different thicknesses were thermally deposited by using a high vacuum coating unit (model E 306 A, Edwards Co., England). Ph-HPQ and Ch-HPQ were sublimated by using a quartz crucible that was subjected to induction heating by a molybdenum heater in a vacuum of 5×10^{-4} Pa. The deposition rate and the films thickness were controlled during the evaporation process by using a quartz crystal thickness monitor (model, TM-350 Maxtek, Inc.,USA). The thin films were sandwiched between two gold electrodes for electrical measurements. The Ohmic contacts of the Au/Ph-HPQ and Au/Ch-HPQ organic compounds were checked by studying the *I–V* characteristics and the results showed that the contact between Au and Ph-HPQ or Ch-HPQ film is Ohmic and no hysteresis or rectification occurred even at high temperatures. The gold electrodes were thermally evaporated directly from a boat-shaped molybdenum filament. The film thickness d is 500 nm and the effective area A is 2.46×10^{-6} m^2 for the two compounds.

2.2. AC electrical measurements

The two-point probes technique was used in electrical measurements for the thin films in sandwich structure (Au/Ph-HPQ/Au) and (Au/Ch-HPQ/Au). The temperature of the sample was recorded during the electrical measurements by using a NiCr–NiAl thermocouple. All measurements were performed in the dark at different temperatures in air.

The AC parameters such as capacitance C, conductance G, and dissipation factor $\tan\delta$ of the films were measured using a programmable automatic LCR bridge (model Hioki 3532 Hitester, Japan). The measurements were carried out in the parallel circuit mode. The measurements were performed in the temperature and frequency ranges of 290–443 K and 0.5 kHz–5 MHz, respectively. The AC conductivity of the samples was estimated from the dielectric parameters. As long as the pure charge transport mechanism is the major contributor to the loss mechanism, the AC conductivity can be calculated using the relation[23]

$$\sigma_{\rm ac}(\omega, T) = \varepsilon_0 \omega \varepsilon_2, \tag{1}$$

where ω is the angular frequency, ε_2 is the imaginary part of the dielectric constant, and ε_0 is the permittivity of free space. The dielectric constant ε_2 is calculated using the relation

$$\varepsilon_2 = \varepsilon_1 \tan\delta, \tag{2}$$

where ε_1 is the real part of the dielectric constant and is calculated using the relation

$$\varepsilon_1 = c\frac{d}{\varepsilon_0 A}. \tag{3}$$

3. Results and discussion

3.1. Frequency dependence of AC conductivity

The dependence of AC conductivity $\sigma_{\rm ac}(\omega, T)$ on frequency for the films of compounds Ph-HPQ and Ch-HPQ at various temperatures is shown in Fig. 2. The effect of the phenoxyphenyl substitution group, as a strong electron donating group, is observed in the $\sigma_{\rm ac}(\omega, T)$ of both compounds and the $\sigma_{\rm ac}(\omega, T)$ of Ph-HPQ is greater than its counterpart of Ch-HPQ. The conductivity curves show two regions: at low frequencies, the increasing rate of $\sigma_{\rm ac}(\omega, T)$ with frequency is slightly lower, and at high frequencies, $\sigma_{\rm ac}(\omega, T)$ increases rapidly with frequency. Depending on the temperature, the change occurs at a particular frequency known as the hopping

frequency ω_p. Also, ω_p increases with increasing temperature in both compounds, indicating their semiconductor behavior. This behavior has been observed in other compounds.[24–26] The observed variation of $\ln\sigma_{ac}$ versus $\ln\omega$ at low frequencies may be explained by adopting the Summerfield theory for hopping conductivity.[27] The theory predicts a scaling law for the low-frequency conductivity

$$\sigma(\omega,T)=\sigma_{dc}\left[1+(\omega/\omega_p)^{\beta}\right], \tag{4}$$

where β is a factor whose value is smaller than 1. The values of σ_{dc}, ω_p, and β are listed in Table 1. At room temperature, the influence of the chlorophenyl substitution group on σ_{dc} and ω_p is greater than that of the phenoxyphenyl substitution group; the value of β for the phenoxyphenyl substitution group is larger than that for the chlorophenyl substitution group. Increasing the annealing temperature increases both σ_{dc} and ω_p and decreases β for both compounds.

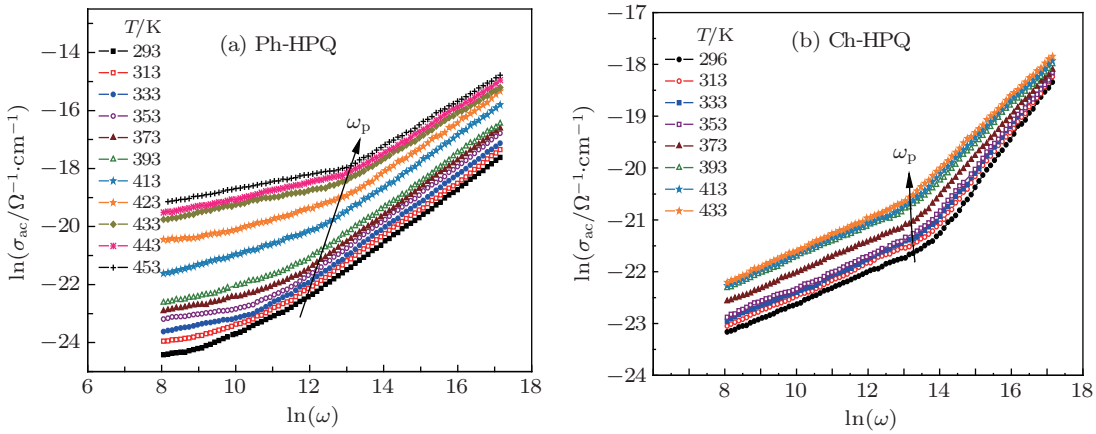


Fig. 2. (color online) Frequency dependence of the AC electrical conductivity for (a) Ph-HPQ and (b) Ch -HPQ at various temperatures.

Table 1. Temperature dependence of various parameters.

T/K	Ph-HPQ			Ch-HPQ		
	$\sigma_{DC}/10^{-11}$ $\Omega^{-1}\cdot$cm^{-1}	ω_p/kHz	β	$\sigma_{DC}/10^{-11}$ $\Omega^{-1}\cdot$cm^{-1}	ω_p/kHz	β
293	0.145	52	0.43	0.602	551	0.38
313	0.32	56	0.36	0.68	638	0.35
333	0.69	64	0.34	0.83	652	0.33
353	1.43	74	0.32	1.02	655	0.32
373	2.6	105	0.3	1.39	659	0.31
393	4.79	112	0.31	2.08	666	0.3
413	13	207	0.36	2.64	670	0.295
423	25	382	0.31	3.42	680	0.29
433	55	464	0.25	4.67	700	0.28
443	113	530	0.245	–	–	–
453	221	577	0.24	–	–	–

At high frequencies, it is found that $\sigma_{ac}(\omega,T)$ is strongly frequency dependent. By plotting $\ln\sigma_{ac}(\omega)$ versus $\ln\omega$ at different temperatures, straight lines are obtained, indicating that the empirical equation[28]

$$\sigma_{ac}(\omega,T)=A'(T)\,\omega^{s(T)} \tag{5}$$

is the most probable one for describing such a behavior, where $A'(T)$ is a constant and $s(T)$ is a factor whose magnitude and dependence on temperature determine the operating conduction mechanism.

The frequency exponents s for the Ph-HPQ and Ch-HPQ compounds are calculated from the slopes of the straight lines of Fig. 2 in the high frequency region. These values are plotted as a function of temperature in Fig. 3. It is clear from Fig. 3 that s-values for Ph-HPQ and Ch-HPQ decrease with increasing temperature. According to the correlated barrier hopping (CBH) model, the frequency exponent s increases towards unity as T tends to 0 K.[29] Therefore, the frequency dependence of $\sigma_{ac}(\omega,T)$ for the studied Ph-HPQ and Ch-HPQ can be interpreted on the bases of the CBH model. The CBH model for AC conductivity was developed initially by Pike[30] for single electron hopping. This model has been extended by Elliott to a two-electron hopping model.[31,32] For neighboring sites at a separation R_ω, the Coulomb wells overlap, resulting in lowering the effective barrier from its maximum height W_M to a value W given by[31]

$$W = W_{\mathrm{M}} - \frac{e^2}{\pi\varepsilon_1\varepsilon_0 R_\omega}, \tag{6}$$

where e is the electron charge and R_ω is the hopping distance given as

$$R_\omega = \frac{e^2}{\pi\varepsilon_1\varepsilon_0\left[W_{\mathrm{M}} + k_{\mathrm{B}}T\left(\ln\left(\omega\tau_0\right)\right)\right]}, \tag{7}$$

where τ_0 is the characteristic relaxation time and is in the order of the atomic vibration period 10^{-13} s,[33] and k_{B} is the Boltzmann constant. In the context of this model, $\sigma_{\mathrm{ac}}(\omega, T)$ is given by the following expression:[31]

$$\sigma_{\mathrm{ac}}\left(\omega, T\right) = \frac{\pi^3}{24}N^2\varepsilon_1\varepsilon_0\omega R_\omega^6, \tag{8}$$

where N is the density of localized states at which carriers exist. The frequency exponent s, according to this model, is evaluated as

$$s = 1 - \frac{6k_{\mathrm{B}}T}{W_{\mathrm{M}} + k_{\mathrm{B}}T\left(\ln\left(\omega\tau_0\right)\right)}. \tag{9}$$

Thus, to a first approximation, it reduces to the simple expression

$$s = 1 - \frac{6k_{\mathrm{B}}T}{W_{\mathrm{M}}}. \tag{10}$$

By using Eq. (10), the average value of the maximum barrier height W_{M} is determined to be 1.13 eV and 1.68 eV for the Ph-HPQ and Ch-HPQ compounds, respectively. The phenoxyphenyl substitution group has a greater reducing effect on the maximum barrier height than the chlorophenyl group. The values of W_{M} are less than the energy gaps of Ph-HPQ and Ch-HPQ. The determined energy gaps from the optical measurements for Ph-HPQ and Ch-HPQ are 2.65 eV and 2.95 eV, respectively.[34] El-Nahass *et al.*[35] attributed the variation in the maximum barrier height to the structural characteristics of the material such as the average grain size, orientation, defect distribution, phase content, and charge carrier density in the organic semiconductors. In this work, the difference in the maximum barrier height is attributed to the influence of the substitution group. The phenoxyphenyl group has a different molecular structure from the chlorophenyl group as shown in Fig. 1, and it is a stronger donating group; therefore, it influences the charge carriers' density and the defect distribution in the matrix. The XRD patterns and AFM images of both compounds in pristine thin film forms showed that they are nanocrystallites dispersed in an amorphous matrix[34] and they differ only in the volume of crystallite size and the volume fraction; the crystallite size and the volume fraction are greater in the Ph-HPQ compound than those in the Ch-HPQ compound.

Figures 4 and 5 illustrate the dependence of the barrier height W on the frequency and temperature for the Ph-HPQ and Ch-HPQ compounds. Both compounds have the same response to the frequency and temperature, where W decreases with increasing frequency but increases with increasing temperature. The dependence of hopping distance R_ω on the frequency for the Ph-HPQ and Ch-HPQ films at various temperatures is shown in Figs. 6 and 7. The hopping distance in both compounds decreases with increasing frequency and temperature. Figures 8 and 9 show the dependence of N on the frequency and temperature for the Ph-HPQ and Ch-HPQ films, respectively. The R_ω behavior is in good agreement with the increment of N as the frequency and temperature increase, such a behavior has been observed in many other compounds.[26,36,37]

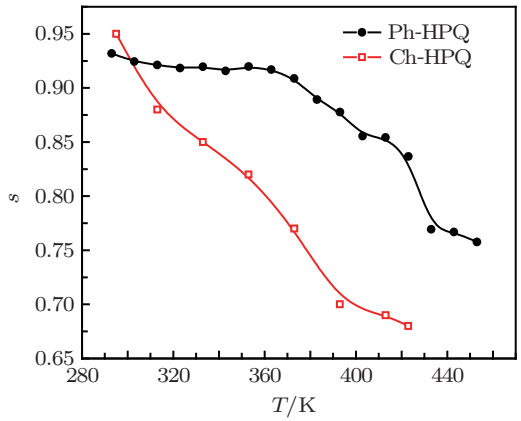


Fig. 3. (color online) Variation of the frequency exponent s with temperature for (a) Ph-HPQ and (b) Ch-HPQ.

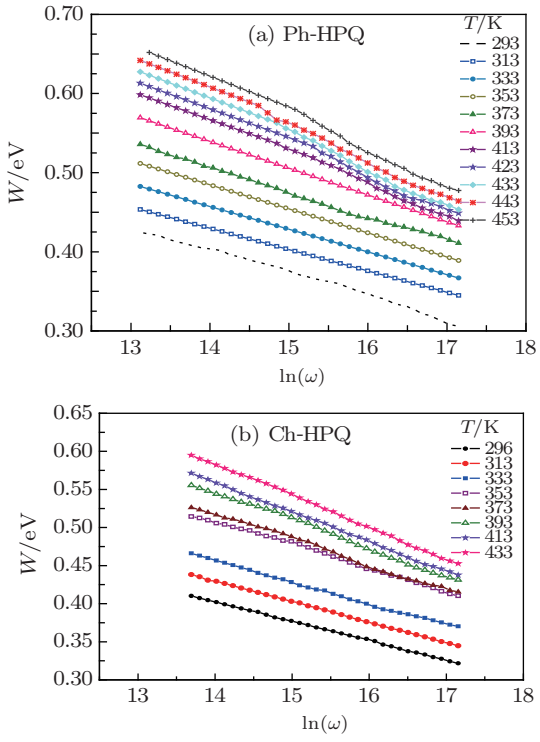


Fig. 4. (color online) Frequency dependence of the barrier height W for (a) Ph-HPQ and (b) Ch- HPQ at various temperatures.

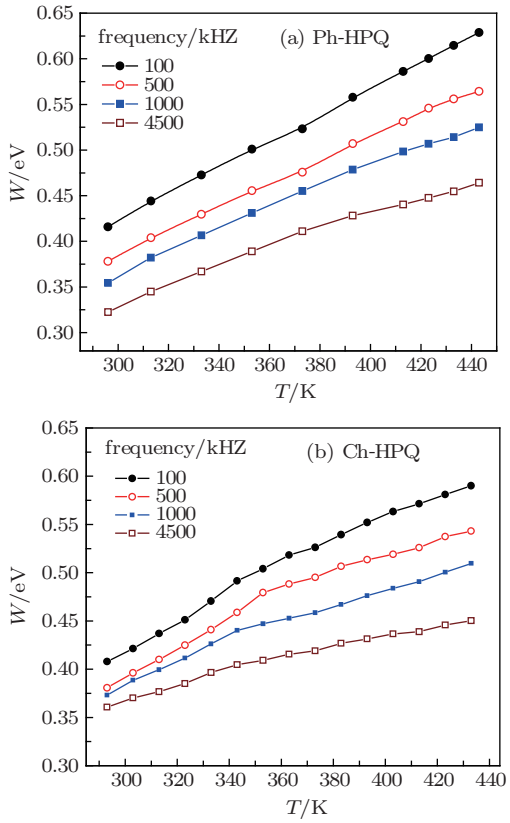


Fig. 5. (color online) Temperature dependence of the barrier height W for (a) Ph-HPQ and (b) Ch-HPQ at various frequencies.

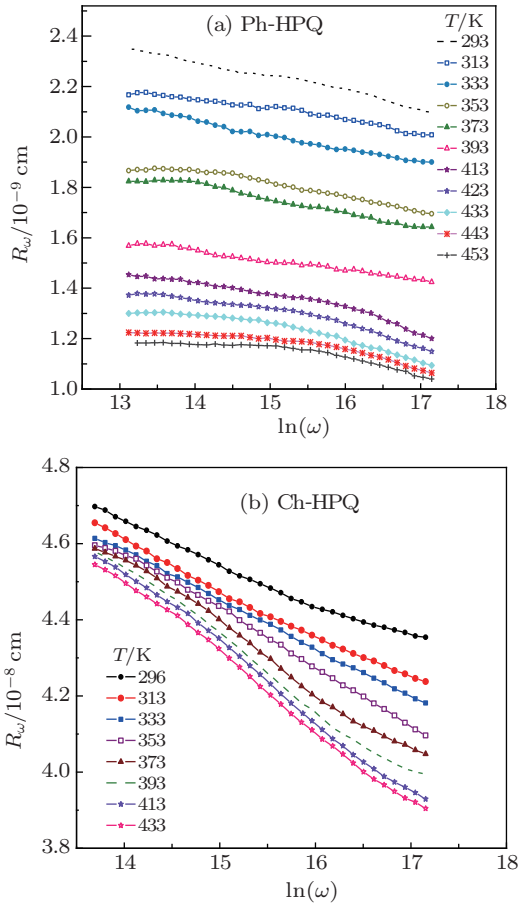


Fig. 6. (color online) Frequency dependence of the hopping distance R_ω for (a) Ph-HPQ and (b) Ch- HPQ at various temperatures.

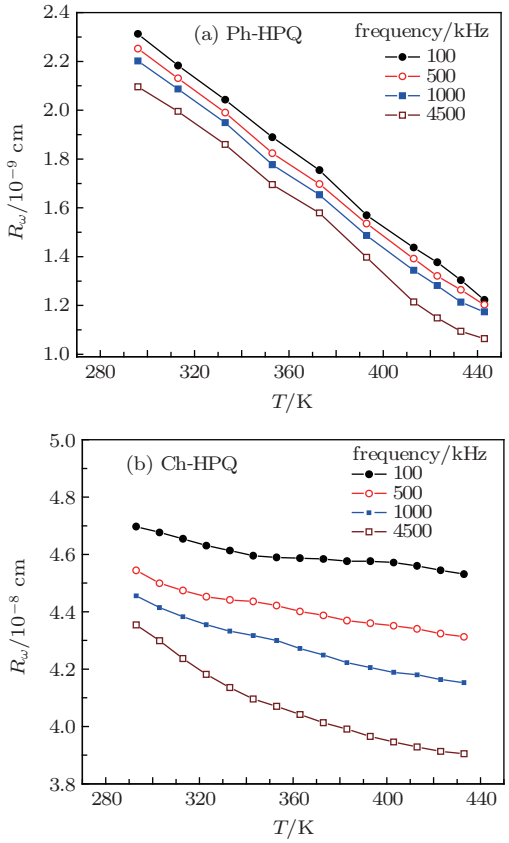


Fig. 7. (color online) Temperature dependence of the hopping distance R_ω for (a) Ph-HPQ and (b) Ch-HPQ at various frequencies.

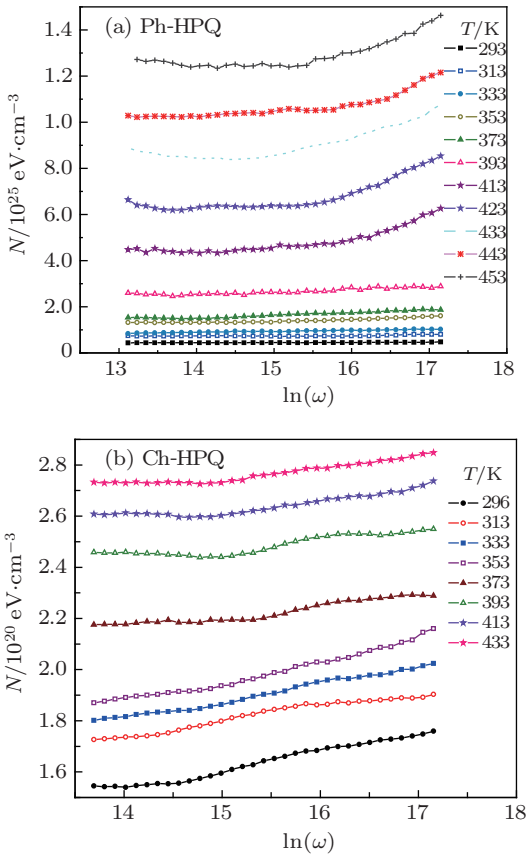


Fig. 8. (color online) Frequency dependence of the density of charges N for (a) Ph-HPQ and (b) Ch-HPQ at various temperatures.

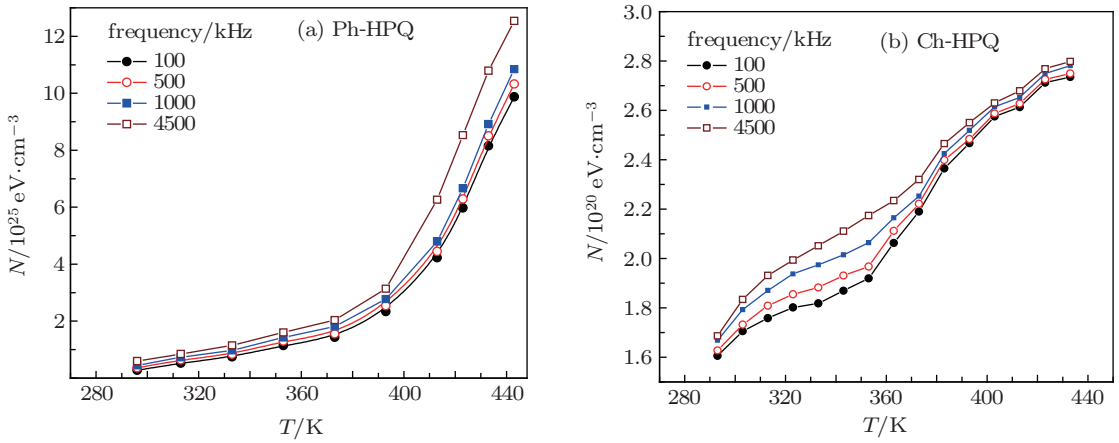


Fig. 9. (color online) Temperature dependence of the density of charges N for (a) Ph-HPQ and (b) Ch-HPQ at various frequencies.

It is obvious that increasing the frequency increases the density of the charges N and decreases the barrier height W; consequently, the charges can jump easily to the nearest neighbor sites in agreement with the results in Refs. [36] and [38]; hence $\sigma_{ac}(\omega,T)$ is increased. Table 2 shows a comparison of those parameters for a given temperature and frequency for the Ph-HPQ and Ch-HPQ films. The density of the charges N as well as $\sigma_{ac}(\omega,T)$ for the Ph-HPQ film at room temperature and frequencies of 10 kHz and 5 MHz is greater than that for the Ch-HPQ film. This can be attributed to the effect of the structure and the strong donation of the phenoxyphenyl group. The presence of the phenyl ring reduces W and R_ω, causing the charges to jump easily to the nearest neighbor sites. Increasing the frequency to 5 MHz increases the values of σ_{ac}, W, R_ω, and N.

Table 2. The AC conductivity $\sigma_{ac}(\omega,T)$, barrier height W, hopping distance R_ω, and the density of the charges N of the Ph-HPQ and Ch-HPQ compounds films for given temperatures and frequencies.

Compound	at 10 kHz & 300 K				at 5000 kHz & 300 K			
	$\sigma_{ac}/10^{-10}$ Ω^{-1}·cm^{-1}	W/eV	$R_\omega/10^{-9}$ cm	N/eV·cm^{-3}	$\sigma_{ac}/10^{-8}$ Ω^{-1}·cm^{-1}	W/eV	$R_\omega/10^{-9}$ cm	N/eV·cm^{-3}
Ph-PHQ	2.2	0.4	2.371	4.4×10^{24}	1.4	0.3	2	4.72×10^{24}
Ch-PHQ	1	0.41	469	0.54×10^{20}	1	0.32	435	1.76×10^{20}

3.2. Temperature dependence of AC conductivity

The dependence of AC conductivity $\sigma_{ac}(\omega,T)$ on the temperature of the Ph-HPQ and Ch-HPQ thin films at different frequencies is shown in Fig. 10. The DC conductivity $(\ln(\sigma_{dc}))$ is also included in Fig. 10 for comparison. It is clear from this figure that the logarithm of the electrical conductivity increases linearly with increasing temperature, demonstrating a typical semiconductor behavior. When σ_{dc} of the films is compared to $\sigma_{ac}(\omega)$ at certain temperature, it is seen that $\sigma_{ac}(\omega,T)$ is higher than σ_{dc}. This is due to the charge carriers in the DC conduction choose the easiest paths which include some large jumps, while this is not so important in the AC conduction.[39] The temperature dependence of AC conductivity $\sigma_{ac}(\omega,T)$ is larger at high frequencies than that at relatively low frequencies. For the two compounds, the relation exhibits two distinct regions separated by a transition temperature; each region has its own slope.

The data in Fig. 10 implies that σ_{ac} is related to the temperature by the Arrhenius law[40]

$$\sigma = \sigma_0 \exp(-\Delta E/k_B T), \qquad (11)$$

where σ_0 is the pre-exponential factor. The activation energies ΔE_I and ΔE_{II} at low and relatively high temperatures respectively for selected frequencies are calculated from the slopes of the linear portions in Fig. 10 together with Eq. (11). Figure 11 depicts the activation energy as a function of temperature for both compounds. The activation energy for the Ph-PHQ compound is greater than its counterpart for the Ch-PHQ compound. The small values of the activation energy confirm that the hopping conduction is the dominant current transport mechanism.[41] It is found that ΔE decreases with increasing frequency as illustrated in Fig. 11. Okutan *et al.*[18] suggested that the applied frequency enhances the electronic jumps between the localized states, and that is why the activation energy decreases with increasing frequency. This result is in good agreement with the decrease in barrier height W and the increase in N with increasing frequency, as demonstrated in Figs. 4 and 8.

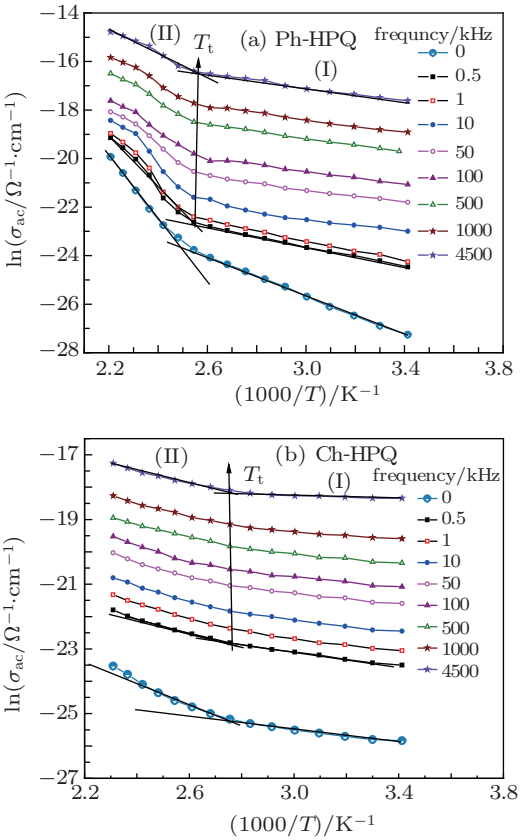


Fig. 10. (color online) Temperature dependence of DC and AC conductivity at different frequencies for (a) Ph-HPQ and (b) Ch-HPQ thin films.

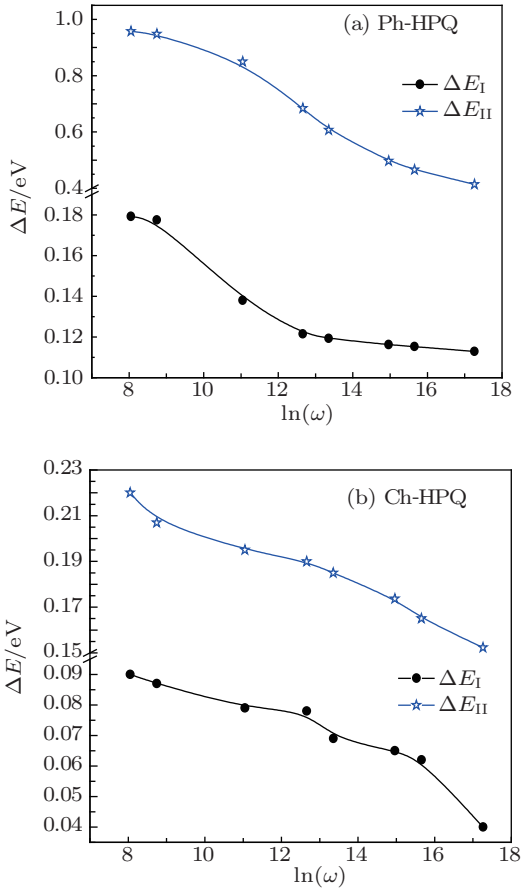


Fig. 11. (color online) Frequency dependence of the AC activation energy for (a) Ph-HPQ and (b) Ch-HPQ thin films.

3.3. Complex impedance spectroscopy

The complex impedance $Z^*(\omega)$ is given by

$$Z^*(\omega) = Z'(\omega) - jZ''(\omega), \tag{12}$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of the complex impedance and are expressed as[42]

$$Z' = \frac{G}{G^2 + \omega^2 C^2}, \tag{13}$$

$$Z'' = \frac{\omega C}{G^2 + \omega^2 C^2}, \tag{14}$$

where G and C are the measured parallel conductance and the capacitance, respectively. The impedance data of the Ph-HPQ and Ch-HPQ thin films are presented in the Nyquist diagram (Z' vs Z''), as shown in Fig. 12. In this figure, the shapes of the plots tend to be straight lines at low temperatures. The slopes of the lines decrease upon increasing temperature. An arc semicircle behavior is observed at relatively high temperatures. The intersection of the curves with the Z'' axis at low temperatures and the arc semicircle behavior indicate the presence of both localized and non-localized conduction processes.[42–46] The Nyquist diagrams of the two compounds have the same behavior. Table 3 shows a comparison of the real and imaginary impedances at the same frequency and temperature for the two compounds. The only difference is that the Ch-HPQ compound has higher real and imaginary impedances than the Ph-HPQ compound.

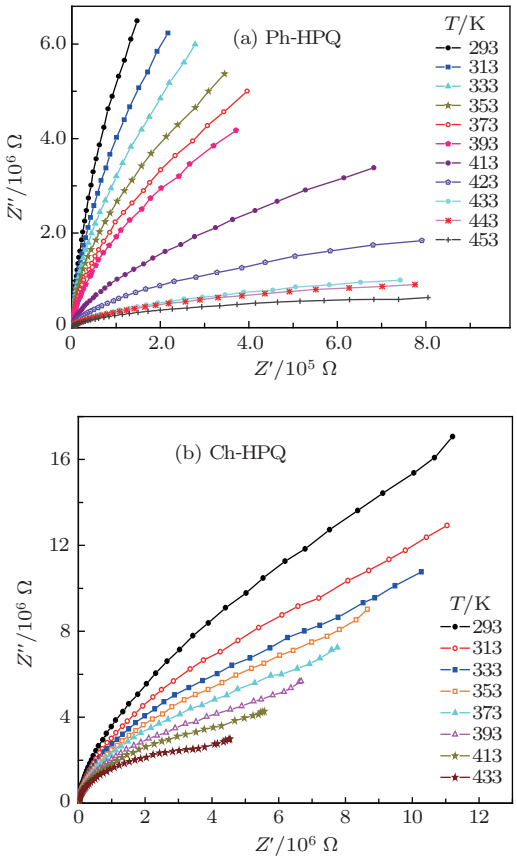


Fig. 12. (color online) Complex impedance plane plots for (a) Ph-HPQ and (b) Ch-HPQ at different temperatures.

Table 3. The complex impedance and the dielectric parameters of the Ph-HPQ and Ch-HPQ films at the same condition of temperature and frequency.

Compound	at 0.5 kHz & 293 K				at 10 kHz & 293 K				at 5000 kHz & 293 K			
	Z' 10^5	$Z''/10^6$	ε_1	ε_2	$Z'/10^4$	$Z''/10^5$	ε_1	$\varepsilon_2/10^2$	Z'	$Z''/10^3$	ε_1	$\varepsilon_2/10^3$
Ph-PHQ	1.47	6.49	3.92	0.19	0.39	5.22	2.2	3	6.5	1.44	2	9
Ch-PHQ	112	17	0.29	0.09	34	18	0.18	1	36	4.98	0.16	1

3.4. Frequency and temperature dependence of dielectric constant

The dielectric properties of the Ph-HPQ and Ch-HPQ thin films were investigated in the frequency range 0.5–5000 kHz. The frequency and temperature dependences of ε_1 for Ph-HPQ and Ch-HPQ were measured nearly in the same temperature and frequency ranges. These dependencies are shown in Fig. 13, which shows that ε_1 decreases with increasing frequency at a constant temperature. Increasing the applied field frequency decreases the orientation polarization, since it takes a longer time than the electronic and ionic polarizations. Such a decrease reduces the dielectric constant ε_1 with increasing frequency.[41] The ε_1 increases with increasing temperature at a constant frequency. The increase of ε_1 with temperature is due to the fact that dipoles in polar materials cannot orient themselves in the direction of the applied field at low temperatures.[47] When the temperature is increased, the orientation of the dipoles is facilitated and thus the orientation polarization increases, which increases ε_1.[47,48] Table 3 and figure 13 illustrate that the values of ε_1 for Ph-HPQ are higher than those for Ch-HPQ at the same condition of temperature and frequency.

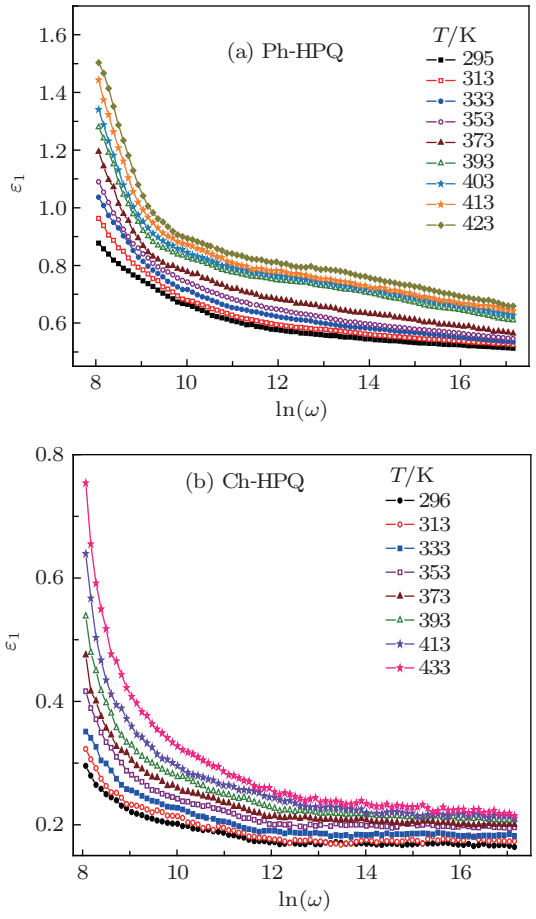


Fig. 13. (color online) Frequency dependence of the real part of the dielectric constant, ε_1, for (a) Ph-HPQ and (b) Ch-HPQ at different temperatures.

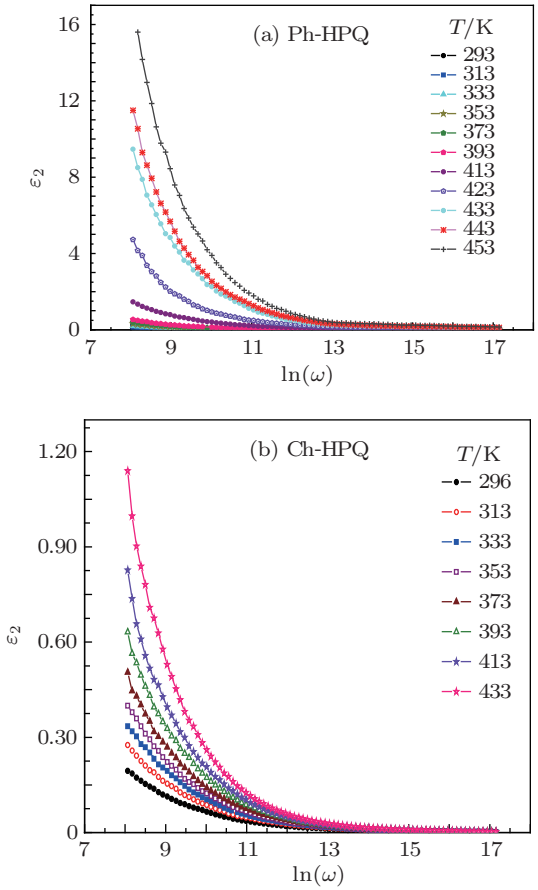


Fig. 14. (color online) Frequency dependence of the imaginary part of dielectric constant, ε_2, for (a) Ph-HPQ and (b) Ch-HPQ at different temperatures.

The dependence of dielectric loss ε_2 on frequency at different temperatures for the Ph-HPQ and Ch-HPQ thin films is shown in Fig. 14. It shows that ε_2 increases with increasing temperature. The imaginary part, ε_2, of the dielectric constant corresponds to a current density within the dielectric that is no longer exactly $\pi/2$ out of phase with the electric field. It is responsible for the dissipation in the dielectric at the specific frequencies as depicted in Fig. 14. The losses that are attributed to conduction presumably involve the migration of ions over large distances. This motion is the same as that occurring under DC conditions where the ions jump over the highest barrier in the network. As the ions move, they dissipate some of their energy to the lattice as heat.[49] Table 3 and figure 14 illustrate

that ε_2 of Ph-HPQ is higher than that of Ch-HPQ for a given temperature and frequency.

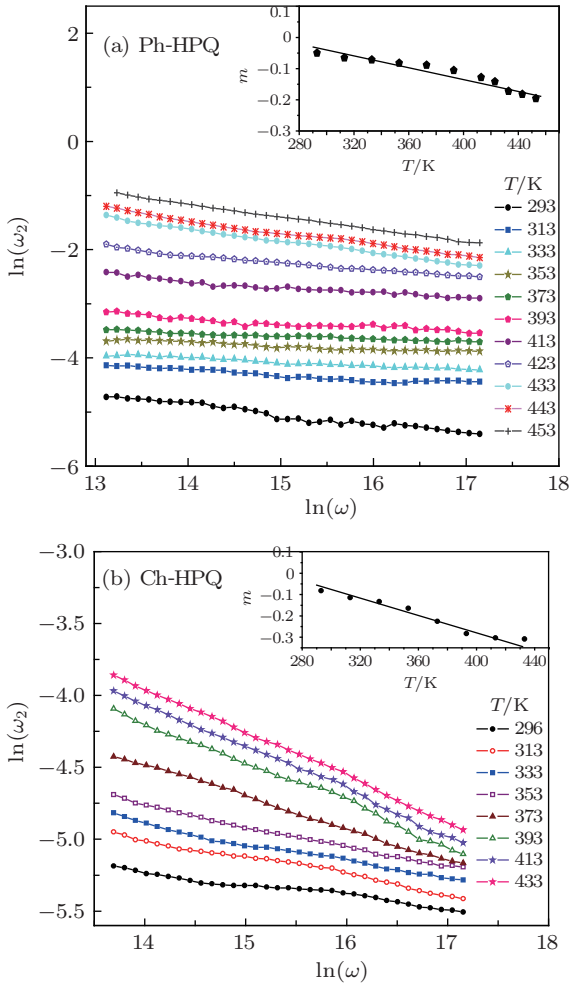


Fig. 15. (color online) Plot of $\ln(\varepsilon_2)$ versus $\ln\omega$ at different temperatures for (a) Ph-HPQ and (b) Ch-HPQ thin films. Inset shows the variation of m with temperature.

Figure 14 shows that ε_2 decreases with increasing frequency. The decrease in ε_2 with increasing frequency can be interpreted as follows. At low frequencies, ε_2 is due to the migration of the ions in the material. At moderate frequencies ε_2 is due to the contribution of ion jump, conduction loss of ion migration, and ion polarization loss. At high frequencies, the ion vibrations may be the only source of the dielectric loss, so ε_2 is frequency independent.[50] The variation of $\ln\varepsilon_2$ with $\ln\omega$ at different temperatures for the Ph-HPQ and Ch-HPQ thin films is shown in Fig. 15. The relation exhibits a series of straight lines with different slopes. The behavior of ε_2 as a function of both frequency and temperature can be analyzed according to the Giuntini model.[51] According to this model, the imaginary part of the dielectric constant is expressed as

$$\varepsilon_2 = A\omega^m, \tag{15}$$

with

$$m = -\frac{4k_{\mathrm{B}}T}{W_{\mathrm{M}}}, \tag{16}$$

where A is a constant and m is a power factor calculated from the slopes of the straight lines in Fig. 15. The inset of Fig. 15 illustrates the variation of m with temperature. It is clear from this figure that m decreases linearly with increasing temperature. The maximum barrier height W_{M} is calculated from the m values at different temperatures using Eq. (16). The average values of W_{M} are 1.28 eV and 0.9 eV for Ph-HPQ and Ch-HPQ, respectively.

4. Conclusions

The substitution group influences the AC conductivity and the dielectric properties of the HPQ compound thin films. The AC conductivity increases with both increasing frequency (0.5 kHz–5 MHz) and temperature (290–443 K). The variation of the AC conductivity of both compounds with frequency is explained in the light of the Summerfield theory for hopping conductivity at low temperatures. Some temperature dependent parameters are calculated. The results also prove that the CBH conduction mechanism is dominant in both compounds. This result is also confirmed by impedance spectroscopy. It is found that the average maximum barrier height is 1.38 eV and 1.68 eV for Ph-HPQ and Ch-HPQ, respectively. The barrier height in both compounds decreases with increasing frequency but increases with increasing temperature. The hopping distance in both compounds decreases with increasing frequency and temperature. The temperature dependence of the AC conductivity shows two activation energies. The variation of the real and imaginary parts of the dielectric constant with temperature and frequency is discussed in the light of the polarization mechanism in the materials. The calculated average maximum barrier height W_{M} is 1.28 eV and 0.9 eV for Ph-HPQ and Ch-HPQ, respectively. In summary, the AC conductivity and the dielectric properties of the HPQ compound thin films depend on the substitution group.

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