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Charge-Transfer Interaction of Aromatic Thiols with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone: Spectral and Quantum Mechanical Studies

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Charge-transfer (CT) complexes formed between aromatic thiol donors (thiophenol (TP), benzene-1,4-dithiol (BDT), *p*-aminothiophenol (ATP), *p*-hydroxythiophenol (HTP), and *p*-toluenethiol (TTP)) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as an acceptor were studied spectrophotometrically in dichloromethane. Addition of aromatic thiols in dichloromethane to DDQ leads to the formation of colored solutions that exhibit a very broad absorption band in the range 440−800 nm and a band in the region 300−400 nm. On the basis of the energies of LUMO and HOMO from quantum mechanical calculations, the broad band observed in the visible region was assigned to the $\pi^*(a_2) \leftarrow \pi(b_1)$ transition and a band observed between 300 and 400 nm was assigned to the $\pi^*(a_2) \leftarrow \pi(a_2)$ transition. The solid CT complexes of aromatic thiols and DDQ were prepared and characterized by FT-IR spectroscopy. The stoichiometry of the CT complexes was determined by Job's continuous variation method. The association constant (K_{CT}), molar extinction coefficient (ϵ), oscillator strength (f), and transition dipole moment (μ) values were calculated from the electronic spectra. The vertical ionization potentials (I^D) of the donors were calculated from their corresponding λ_{CT}. Quantum mechanical (QM) calculations were performed to determine the ionization potential and the energies of the highest occupied molecular orbital (HOMO) of donors and lowest unoccupied molecular orbital (LUMO) of an acceptor.

1. Introduction

Studies on electron donor−acceptor (EDA) or charge-transfer (CT) complexes have received much attention in recent years because of their wide applications ranging from chemistry, materials science, and medicine to biology.[1−5] Recently, research on molecular electronics is also gaining momentum mainly due to the revolution in the miniaturization of electronic systems.[6,7] Thiol-derivatized oligo(phenylenethynylene) molecules are widely used as molecular wires because thiol groups can make a covalent bond with metal surfaces like gold.[8,9] To improve the conductivity of these molecular wires, several strategies have been reported in the literature.[10−12] The formation of a surface-confined CT complex is demonstrated by the reaction of a strong electron acceptor, tetracyanoethylene with a self-assembled monolayer (SAM) of an electron donor, tetramethylxylenedithiol (TMX), and resulting in a 50-fold increase in the conductivity when compared to the SAM of TMX alone.[13] Because the sulfur atom of the thiol group has two lone pairs of electrons, it is expected to behave as a donor molecule.[14,15] On the other hand, the π-orbitals of the benzene nucleus in thiol derivatives also have a donor property. Quinone derivatives are well-known for their π-acceptor property because they have an empty π^* orbital (LUMO).[16,17] Therefore studies on the electron transfer between them are important for the fabrication of conducting materials useful in future molecular electronic applications.[18] Although CT complexes of phenolic and aniline derivatives with different acceptors have been studied extensively,[19] only a few reports have been published on CT complexes of thiol derivatives with different acceptors.[20−24] In the present study, we are focusing on the CT interaction of aromatic thiols such as thiophenol (TP), benzene-1,4-dithiol (BDT), *p*-aminothiophenol (ATP), *p*-hydroxythiophenol (HTP), and *p*-toluenethiol (TTP) (**1**−**5**) as donors with acceptor 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (Chart 1). The present study involves the investigation of the electronic and vibrational spectral characteristics of the formed CT complexes and determination of the nature of forces responsible for the stabilization of the complexes. Quantum mechanical (QM) calculations are performed to determine the ionization potential and the energies of highest occupied molecular orbital (HOMO) of donors and lowest unoccupied molecular orbital (LUMO) of acceptor.

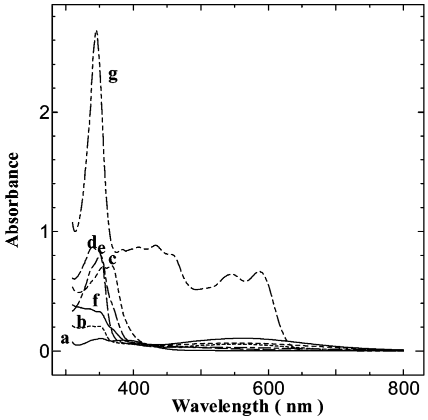

Figure 1. Absorption spectra of (a) DDQ and CT complexes of DDQ with (b) TP, (c) BDT, (d) ATP, (e) HTP, (f) TTP, and (g) electrochemically generated DDQ$^{\bullet-}$ in solution

2. Materials and Methods

Dichloromethane and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (E. Merck, India) and thiophenol (TP), benzene-1,4-dithiol (BDT), *p*-aminothiophenol (ATP), *p*-hydroxythiophenol

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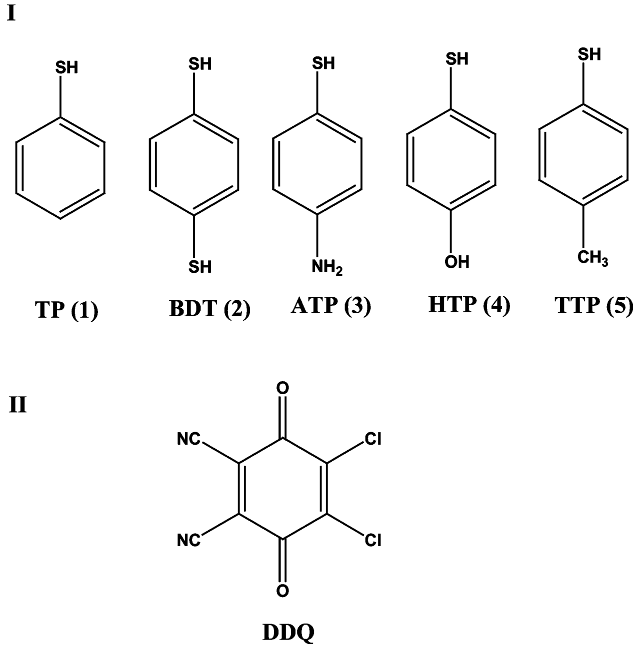
CHART 1: Structures of (I) Donors (TP, BDT, ATP, HTP, and TTP) and (II) Acceptor (DDQ)



TP (1) BDT (2) ATP (3) HTP (4) TTP (5)

DDQ

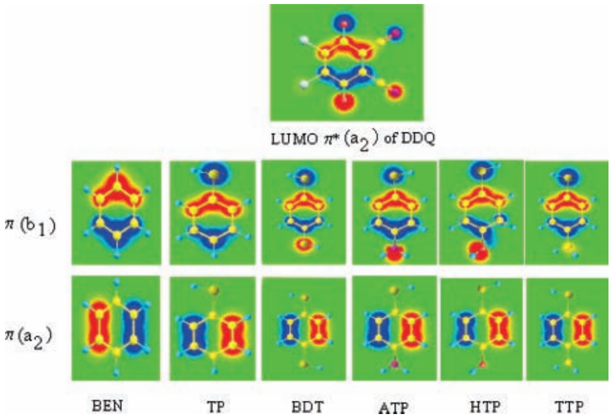


Figure 2. Molecular orbitals of DDQ, benzene (BEN) and aromatic thiols (**1**−**5**).

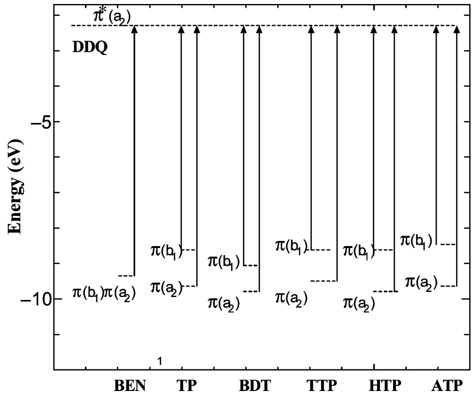


Figure 3. MO energy-level diagrams and transitions of the CT complexes of aromatic thiols (**1**−**5**) and DDQ.

(HTP), and *p*-toluenethiol (TTP) (TCI, Tokyo Kasei, Japan) were used without further purification. All other chemicals used in this work were of analytical grade. The solid CT complexes of DDQ with different aromatic thiols were prepared by mixing 5 mmol of the donor in dichloromethane with 4 mmol of acceptor in the same solvent for 1:1 complex and 10 mmol of the donor in dichloromethane with 4 mmol of acceptor in the same solvent for 2:1 complex. The mixture was stirred at room temperature for 2 h. After evaporation of solvent, solid product was collected and washed with dichloromethane. FT-IR spectra were recorded as KBr disks using a JASCO FT-IR 460 Plus spectrometer. The electronic spectra were recorded using a Perkin-Elmer UV−vis Lambda35 spectrophotometer. To avoid the interference of other bands with the CT band, we have filled the reference cell with the DDQ of the same concentration in the sample cell. Spectroelectrochemical studies were done using platinum wire as working and counter electrodes and silver wire as a reference electrode in a quartz cell containing 1×10^{-4} M DDQ and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte in dichloromethane. Semiempirical calculations were done using MOPAC 2000 version 1.0 at the PM3 level theory. *Ab initio* calculations were done using the Gamess US program by HF model at the 6-311G level of theory. The structures were optimized using same level of theory. The output of the *ab initio* calculations was visualized using ChemCraft 1.5 software.

3. Results and Discussion

3.1. UV−Visible Spectral Studies and QM Calculations of CT Complexes. Mixing dichloromethane solutions of **1**−**5** with DDQ formed colored solutions immediately. Figure 1 shows the UV−vis spectra of DDQ and **1**−**5** with DDQ in dichloromethane. DDQ shows a band at 372 nm (line a) but no absorption band appeared for DDQ and **1**−**5** in the region 440−800 nm. However, the absorption spectra obtained for **1**−**5** with DDQ in dichloromethane solution show a broad absorption band from 440 to 800 nm and a band of DDQ between 300 and 400 nm was enhanced, demonstrating the formation of CT complexes between **1**−**5** and DDQ. The CT absorption band represented in the spectra appeared at 552 nm for DDQ-TP (line b), 547 nm for DDQ-BDT (line c), 461 nm for ATP-DDQ (line d), 529 nm for HTP-DDQ (line e), and 561 nm for DDQ-TTP (line f).

Ab initio and semiempirical calculations were performed for the isolated donors and acceptor. The energies of HOMO of donors and LUMO of the acceptor were calculated without considering the solvent effects. The calculated molecular orbitals (MOs) for the aromatic thiols are shown in Figure 2.

Among the number of filled MOs we consider only the first two HOMOs, which have orbital symmetry with the LUMO of DDQ. Because the benzene molecule has two degenerate π-(e_{1g}) orbitals,[25,26] only one CT band is expected. However, MO’s ($\pi(e_{1g})$) degeneracy will be removed when substituents like thiol, amino, hydroxyl, and methyl are present in the benzene nucleus and these MOs split into $\pi(b_1)$ and $\pi(a_2)$ with the appreciable energy separation depending upon the nature, number, and position of the substituent.[26] The possible CT transitions are shown in Figure 3. It shows that the lowest energy transition is $\pi^*(a_2) \leftarrow \pi(b_1)$. We have calculated the vertical ionization potential of donors (I^D) for the bands observed in the spectra, and present them in Table 1. The values are in good agreement with the theoretical values. Now it is possible to assign the transitions for the CT band including two bands enhanced in the absorbance obtained for **1**−**5** with DDQ (Figure 1). The CT band at 440−800 nm corresponds to $\pi^*(a_2) \leftarrow \pi(b_1)$ (lowest energy band) and the band observed between 300 and 400 nm corresponds to $\pi^*(a_2) \leftarrow \pi(a_2)$ transition. In the present study, we are interested in the broad lowest energy band observed in the 440−800 nm region (Figure 4) corresponding to the $\pi^*(a_2) \leftarrow \pi(b_1)$ transition for detailed investigation.

The broadness of the CT band in Figure 4 is due to the weak $\pi-\pi^*$ interaction[24] between **1**−**5** and DDQ. The noninvolve-

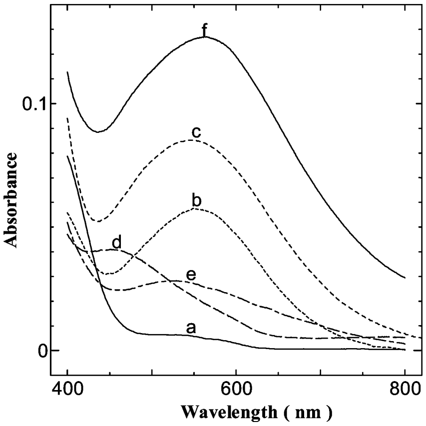


Figure 4. Absorption spectra of (a) DDQ and CT complexes of DDQ with (b) TP, (c) BDT, (d) ATP, (e) HTP, and (f) TTP in the visible region.

TABLE 1: MO Energies and Ionization Potentials of Aromatic Thiols (1−5) and DDQ

	MO energy[a] (eV)			ionization potential[b] (eV)	
compound	$\pi(b_1)$	$\pi(a_2)$	π^* (a_2)	I^D $(\pi^*(a_2) \leftarrow \pi(b_1))$	I^D $(\pi^*(a_2) \leftarrow \pi(a_2))$
TP	−8.6098	−9.6030		8.50	10.12
BDT	−8.9907	−9.8724		8.54	9.85
ATP	−8.5717	−9.5567		9.06	10.13
HTP	−8.6778	−9.7717		8.63	10.09
TTP	−8.5363	−9.4696		8.47	9.87
DDQ			−1.63		

[a] Values obtained from ab initio calculation. [b] Values obtained from the electronic spectra.

ment of the DDQ anion radical in the CT complex formation was confirmed by recording the UV−vis spectrum of 0.1 mM DDQ in dichloromethane after 3 min continuous electrolysis at −0.39 V,[27] and the corresponding spectrum is shown as curve g in Figure 1. It shows the absorption band characteristic of the DDQ anion radical[28] but does not match the broad spectra of CT complexes in the region 440−800 nm, indicating that the DDQ anion radical was not participated in the formation of CT complexes. Further nonparticipation of the DDQ anion radical in the formation of the CT complex is proved by recording ESR spectra for CT complexes of **1**−**5** with DDQ in dichloromethane. It shows no signal corresponding to the DDQ anion[29] (spectrum not shown).

Job's plot[30] was used to determine the composition of the CT complex formed. Figure 5 shows Job's plots of the molar ratio of **1**−**5** and DDQ against absorbance. It was found that TP, TTP, and ATP form 1:1 complexes with DDQ whereas BDT and HTP form 2:1 complexes with DDQ.

3.2. Determination of the Formation Constant. The formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}) of the formed CT complexes in solution were determined using the Scott equations (eqs 1 and 2)[31,32] under the condition of $[A]_o \gg [D]_o$. We were keeping $[A]_o$ as constant and varying $[D]_o$ ($[A]_o$ and $[D]_o$ are the initial concentrations of acceptor and donors, respectively).

$$\frac{[A]_o[D]_o\,1}{A} = \frac{[D]_o}{\epsilon_{CT}} + \frac{1}{K_{CT}\epsilon_{CT}} - \frac{C}{\epsilon_{CT}} \qquad (1)$$

$$\frac{[A]_o[D]_o^{\,2}\,1}{A} = \frac{[D]_o^{\,2}}{\epsilon_{CT}} + \frac{1}{K_{CT}\epsilon_{CT}} - \frac{C}{\epsilon_{CT}} \qquad (2)$$

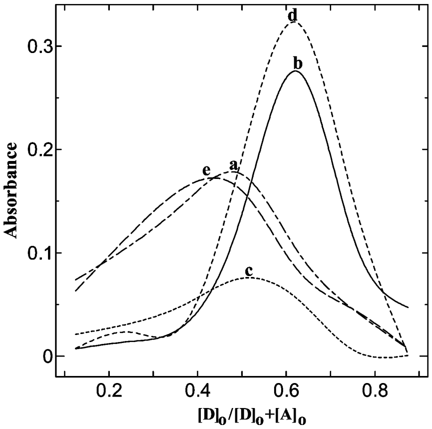


Figure 5. Molar ratio plot of (a) DDQ-TP, (b) DDQ-BDT, (c) DDQ-ATP, (d) DDQ-HTP, and (e) DDQ-TTP.

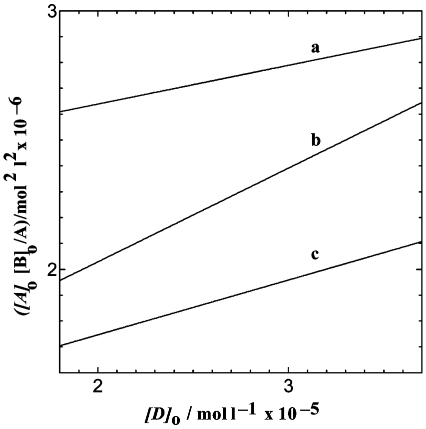


Figure 6. Representative plot of $[D]_o[A]_o/A$ against $[D]_o$ for (a) DDQ-TTP, (b) DDQ-ATP, and (c) DDQ-TP.

TABLE 2: CT Complex Absorption Maxima, Formation Constant and Molar Absorptivities

s. no.	CT complex	color	λ_{max} (nm)	K_{CT} (dm^3 mol^{-1})	ϵ_{max} (dm^3 mol^{-1} cm^{-1})
1	DDQ−TP	purple	552	56 333.90	50.92
2	DDQ−BDT	purple	547	55 570.78	42.76
3	DDQ−ATP	brown	461	28 451.96	27.37
4	DDQ−HTP	purple	529	6318.74	67.57
5	DDQ−TTP	purple	561	16 114.54	47.26

where *A* is the absorbance and *C* is the concentration of the CT complexes in solution. From the plot of $[D]_o$ against the factor $[A]_o[D]_o/A$ in the left-hand side of eq 1 and $[D]_o^2$ against the factor $[A]_o[D]_o^2/A$ in the left-hand side of eq 2, we can calculate K_{CT} and ϵ_{CT} (Figure 6). The calculated values are given in Table 2.

Stabilities of complexes vary with the varying electron-donating ability of the substituents.[33] Because the less electronegative sulfur atoms of thiol facilitate the donor for effective CT interaction with DDQ, the values of formation constants of DDQ-TP and DDQ-BDT are relatively very high in comparison with other CT complexes in Table 2. Although DDQ-ATP has an electron-donating amino group, the K_{CT} value is moderate because the nitrogen atom is more electronegative than the sulfur atom. In the case of DDQ-HTP, the oxygen atom of HTP has a higher electronegativity than sulfur and nitrogen atoms and thus it gives the lowest K_{CT} value. The observed lowest K_{CT} value of DDQ-TTP in comparison with other CT complexes may be due to the steric repulsion of a bulky methyl group present in TTP.

TABLE 3: CT Energy, Ionization Potential, Oscillator Strength, Transition Dipole Moment, and Degree of Charge Transfer of CT Complexes

s. no.	CT complex	E_{CT} (eV)	I^D (eV)[a]	f	μ_{CT} (Debye)	$10^{-3}\rho$
1	DDQ−TP	2.24	8.50 (8.95)	0.0013	1.61	1.44
2	DDQ−BDT	2.26	8.54 (8.54)	0.0731	2.92	1.43
3	DDQ−ATP	2.68	9.06 (8.98)	0.0114	1.01	1.34
4	DDQ−HTP	2.34	8.63 (8.55)	0.0102	1.06	1.41
5	DDQ−TTP	2.20	8.47 (8.66)	0.0073	0.94	1.45

[a] Values in parentheses are theoretically calculated using MOPAC 2000 program.

3.3. Characteristics of CT Complexes. Ionization potentials of the donors (I^D) were calculated by using both the energy of the CT bands and the semiempirical method. I^D can be obtained from the energy of the charge-transfer bands by applying the following empirical equation.[34]

$$I^D\ (\text{eV}) = 5.76 + 1.52 \times 10^{-4} \upsilon\ (\text{cm}^{-1}) \qquad (3)$$

where υ is the wavenumber corresponding to the charge-transfer band. The calculated ionization potential values are given in Table 3. The values calculated from the energy of the CT band are in good agreement with the values calculated from semiempirical method.

The oscillator strength (f), the integrated intensity of an absorption band, which is a dimensionless quantity used to express the transition probability of the CT band[35] and the transition dipole moment (μ_{CT}) of the CT complexes[36] can be defined as

$$f = 4.70 \times 10^{-7}\ \bar{\upsilon}_{max} \mu^2 \qquad (4)$$

$$\mu_{CT} = ab(\mu_1 - \mu_o) \qquad (5)$$

where $\bar{\upsilon}_{max}$ is the frequency in cm^{-1} of maximum intensity of the absorption, μ_{CT} is the transition dipole, a and b are the coefficients of ground-state wave functions of nonbonded and dative structures, respectively. μ_1 and μ_0 are the dipole moments of nonbonded and dative structures, respectively. The dipole moment μ_{CT} is directly related to the measure of the dative contribution to the ground state of complex. Quantitatively, μ_{CT} can be defined as the product of the intermolecular separation of the donor and acceptor in the ground state (r_{AD}), the charge that has transferred as follows[36]

$$\mu = er_{AD} \qquad (6)$$

The oscillator strength and transition dipole moment were calculated experimentally by the following expressions[37,38]

$$f = 4.32 \times 10^{-9} \epsilon_{max} \Delta\bar{\upsilon}_{1/2} \qquad (7)$$

$$\mu_{CT} = 0.0958[\epsilon_{max} \Delta\bar{\upsilon}_{1/2}/\bar{\upsilon}_{max}]^{1/2} \qquad (8)$$

where ϵ_{max} is the maximum molar absorptivity of the band, $\bar{\upsilon}_{1/2}$ is the half-width of the band. Among the CT complexes, DDQ-BDT show the highest μ_{CT} value (Table 3), suggesting that it has a high degree of dative contribution to the ground-state complex. The remaining four CT complexes have moderate dative contribution to their respective ground-state complex.[39] Again, DDQ-BDT shows the highest f value among the CT complexes (Table 3) whereas DDQ-TP shows the lowest f value. The possible reason for the lowest f value of DDQ-TP is the interaction between the excited donor and CT complex molecules, which diminishes the intensity of the CT band.[39]

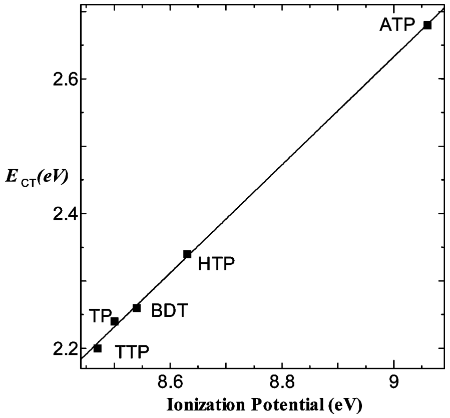


Figure 7. Plot of energy of CT band against ionization potential of aromatic thiols (**1**−**5**).

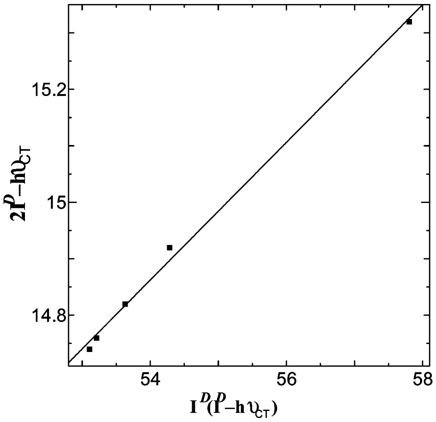


Figure 8. Plot of $2I^D$ - $h\upsilon_{CT}$ against $I^D(I^D - h\upsilon_{CT})$ for DDQ-aromatic thiols (**1**−**5**).

The energy of the charge-transfer complex (E_{CT}) is calculated from the λ_{max} of the CT band, and the values are given in Table 3. Figure 7 shows the plot of ionization potential against CT energies of the complexes. The plot shows a good linearity, suggesting that it is difficult to promote an electron from the donor to acceptor molecule as the I^D of donor increases and hence the energy of the CT band increases. Thus, one can predict either the ionization potential of the aromatic thiols or the CT energy of the complex with DDQ from Figure 7 by knowing any one of the parameters.

3.4. Degree of Charge Transfer. The degree of charge transfer of CT complexes of **1**−**5** and DDQ were evaluated on the basis of Mulliken two-state model.[36,40,41] The ionicity determined by the degrees of charge transfer is one of the most important parameters that determine the electronic and optical properties of the CT complexes.[39] The ground (ψ_g) and excited-state (ψ_e) wave functions of the CT complex are described by a linear combination of no bond $\psi(D°,A°)$ and ionic $\psi(D^+,A^-)$ states.

$$\psi_g = \sqrt{(1-\rho)}\psi_{(D_o,A_o)} + \sqrt{\rho}\psi_{(D^+,A^-)} \qquad (9)$$

$$\psi_g = \sqrt{(1-\rho)}\psi_{(D^+,A^-)} + \sqrt{\rho}\psi_{(D_o,A_o)} \qquad (10)$$

where ρ is the degree of charge transfer from donor to an acceptor.

According to Mulliken's theory, the energy of the CT transition can be expressed as follows[35]

$$h\upsilon_{\mathrm{CT}} = I^{\mathrm{D}} - C_1 + \frac{C_2}{(I^{\mathrm{D}} - C_1)} \qquad (11)$$

$$C_1 = E_{\mathrm{A}} + G_1 + G_{\mathrm{o}} \qquad (12)$$

where C_1 and C_2 are constants for a given acceptor and C_1 consists of vertical electron affinity (E_A)[42] with other energy terms G_1 and G_0. G_0 is the sum of energy terms (like dipole−dipole, Van der Waals interaction, etc.) in the no bond state, and G_1 is the sum of energy terms in the dative state. G_0 can be neglected because it is very small in most of the cases and G_1 is mainly the electrostatic energy of attraction between D^+ and A^- in the dative state. By taking the typical D−A distance in π-type CT complexes to be 3.5 Å the major part of G_1 is estimated to be $e^2/4\pi\epsilon_0 r = 4.13$ eV.[43]

The rearrangement of eq 11 gives the following relation

$$2I^{\mathrm{D}} - h\upsilon_{\mathrm{CT}} = \left(\frac{1}{C_1} I^{\mathrm{D}}(I^{\mathrm{D}} - h\upsilon_{\mathrm{CT}}) + C_1 + \frac{C_2}{C_1}\right) \qquad (13)$$

Using the observed CT energies and vertical ionization potential of donors from the UV−vis spectral studies, we could obtain the correlation (eq 14) with the correlation coefficient of 0.99 (Figure 8). This confirms the CT nature of the transition and the slope of the eq 13 yields $C_1 = 8.2041$ eV and $C_2 = 0.62752$ (eV).[2]

$$2I^{\mathrm{D}} - h\upsilon_{\mathrm{CT}} = (0.1219 \pm 0.00417) I^{\mathrm{D}}(I^{\mathrm{D}} - h\upsilon_{\mathrm{CT}}) + (8.2806 \pm 0.22715) \qquad (14)$$

The degree of charge transfer ρ was calculated using the following relation, and the values are given in Table 3.

$$\rho = \frac{\frac{C_2}{2}}{(I^{\mathrm{D}} - E_{\mathrm{A}} + C_1)^2 + \frac{C_2}{2}} \qquad (15)$$

The relationship between I^D and ρ is shown in Figure 9.

As expected, the degree of charge transfer decreases when the ionization potential of **1**−**5** increases. It shows that the degree of charge transfer from the HOMO of the donor decreases as the ionization potential increases. Further, the very small values of degree of charge transfer indicating that the formed CT complexes are very weak.

3.5. FT-IR Spectral Studies of CT Complexes. FT-IR spectra were recorded for solid CT complexes of **1**−**5** and DDQ. Figures 10 and 11 show the spectra of >C═O and −C≡N stretching bands of CT complexes. In Figures 10 and 11, significant shifts in the stretching frequencies of both −C≡N and >C═O are observed for CT complexes with respect to DDQ, confirming the formation of CT complexes between **1**−**5** and DDQ.

The degree of charge transfer between the aromatic thiols and DDQ can be visualized by the change in the stretching frequencies of −C≡N and >C═O of DDQ.[44,45] Because −C≡N and >C═O groups have conjugation with the >C═C< group, their IR absorptions are more sensitive to electron transfer to the antibonding orbital of >C═C< of DDQ. Due to the flow of electron density from the $\pi(b_1)$ orbital of the benzene nucleus of aromatic thiols to $\pi^*(a_2)$ orbital of the DDQ, the stretching frequency of the −C≡N group increases as the amount of charge that flows into the $\pi^*(a_2)$ orbital of DDQ increases.

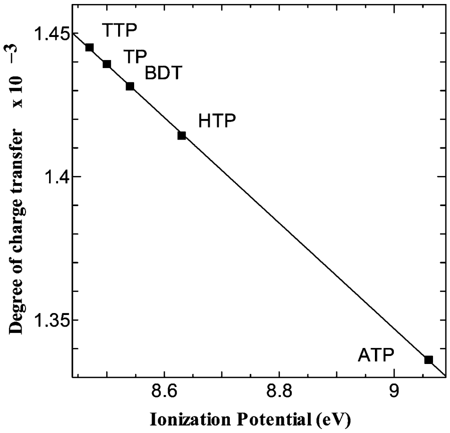


Figure 9. Degree of charge transfer (ρ) for DDQ-aromatic thiols (**1**−**5**) complexes as a function of ionization potential of **1**−**5**.

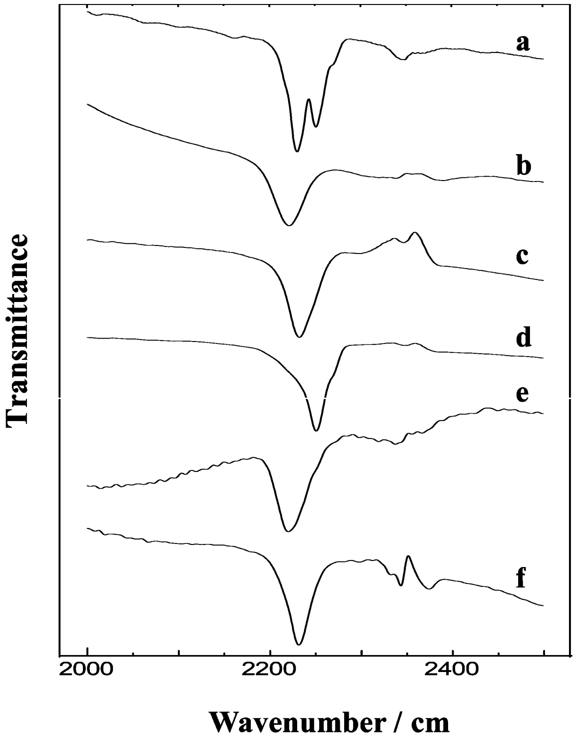


Figure 10. FT-IR spectra of υ_{CN} for (a) DDQ, (b) DDQ-TP, (c) DDQ-BDT, (d) DDQ-ATP, (e) DDQ-HTP, and (f) DDQ-TTP complexes.

This can be seen from Figure 12, as the ionization potential of donors increases, the $\upsilon_{\mathrm{CNstr}}$ also increases. Because the dipole of the DDQ calculated by *ab initio* study lies perpendicular to the axis passing through the >C═O groups, a higher degree of conjugation is expected for −C≡N than for >C═O with >C═C< group. The bond order of >C═C< and −C≡N groups decreases as the charge flow into the $\pi^*(a_2)$ orbital of the >C═C< group increases. In addition to $\upsilon_{\mathrm{CNstr}}$, a significant shift in $\upsilon_{\mathrm{COstr}}$ was also observed due to the charge transfer (Figure 11). $\upsilon_{\mathrm{COstr}}$ decreases as the ionization potential of aromatic thiols increases (Figure 13).

The injection of electron density to the $\pi^*(a_2)$ orbital of the >C═C< group leads to a decrease in the bond order. Thereby, the >C═O bond could lose conjugation with the >C═C< group and the >C═O bond order increases; consequently, $\upsilon_{\mathrm{COstr}}$ increases. The stretching frequency of the >C═O group in the DDQ-HTP CT complex was broadened due to the possible hydrogen bonding between the −O−H or −S−H groups of the aromatic thiol and the >C═O group of the DDQ. The reason

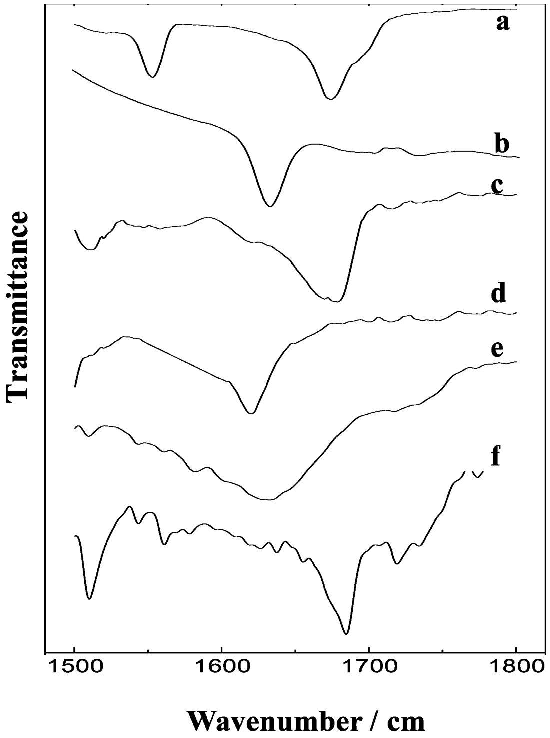


Figure 11. FT-IR spectra of υ_{CO} for (a) DDQ, (b) DDQ-TP, (c) DDQ-BDT, (d) DDQ-ATP, (e) DDQ-HTP, and (f) DDQ-TTP complexes.

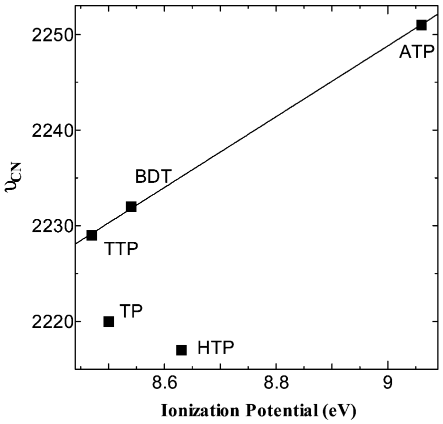


Figure 12. Plot of ionization potential of aromatic thiols (**1**−**5**) against υ_{CN} of CT complexes.

for the deviation of both TP and HTP from the straight line in Figures 12 and 13 is likely that the hydrogen atoms of −S−H and −O−H may interact with the >C═O and −C≡N groups of DDQ through hydrogen bonding. As a result, a significant decrease in the stretching frequencies of both −C≡N and >C═O were observed. A large deviation of TP from the straight line in Figure 13 (~54 cm^{-1}) when compared to Figure 12 (~10 cm^{-1}) suggests that thiol group of TP is more effectively interacting with >C═O than −C≡N. In the case of other CT complexes, the presence of bulky group at the *para* position of aromatic thiols may not favor hydrogen bonding. It is evident from Figures 12 and 13 that the change in υ_{CNstr} and υ_{COstr} depends only on the ionzation potential of the aromatic thiols.

For the DDQ-ATP complex, the $-NH_2$ stretching bands from 3500 to 3300 cm^{-1} (doublet) of the parent base were replaced by a strong broad band at 3200 cm^{-1} (not shown). It shows that both the symmetric and antisymmetric modes of the $-NH_2$ group have merged into one in the complex and may be involved in the hydrogen bonding. The large deviation of υ_{CNstr} and υ_{COstr} of HTP from the straight line in Figures 12 and 13 suggests the interaction of −OH group with DDQ.

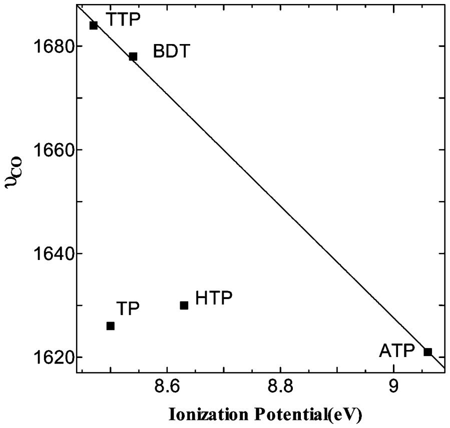


Figure 13. Plot of ionization potential of aromatic thiols (**1**−**5**) against υ_{CO} of CT complexes.

4. Conclusion

The spectral properties of CT complexes of DDQ with different aromatic thiols were established. The spectral and QM studies have shown that the $\pi-\pi^*$ interaction is involved in the CT complex formation between aromatic thiols (**1**−**5**) and DDQ. FT-IR studies of the solid CT complexes indicate that both −C≡N and >C═O groups of DDQ are highly sensitive to charge transfer. The driving force for the CT complex formation is the interaction between the $\pi(b_1)$ orbital of aromatic thiols and the $\pi^*(a_2)$ orbital of DDQ. The CT complexes of TP, HTP, BDT, and ATP with DDQ are stabilized by hydrogen bonding apart from the $\pi-\pi^*$ interaction.

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