UV-vis, IR spectra and Computational studies of charge transfer complex formed between Benzochromene and π-Acceptors.

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Abstract

Three charge-transfer complexes formed between three π-acceptors (picric acid, chloranilic acid and 2,3 – dichloro - 1,4 - naphthquinone) with benzochromene as donor were synthesized and characterized by electronic, IR spectroscopy and elemental analysis. Elemental analysis and photometric titration of investigation demonstrate that the molar ratio of the synthesized charge transfer complexes as 1: 2 ratios (donor: acceptor). The spectroscopic and physical data were estimated using Benesi-Hildebrand and its modification method in terms of formation constant (κ_{CT}), molar extinction coefficient (ε_{CT}), standard free energy (ΔG°), oscillator strength (f), ionization potential (I_p) and transition dipole moment (μ). Determination the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) reveal that charge transfer are within the molecule.

Introduction:-

Mullikan suggested that the formation of molecular complexes from two molecules can arise from a π-molecular orbital of a Lewis base to a vacant π-molecular orbital of a Lewis acid with resonance between the dative structure and no bond structure stabilizing the complex. He also suggested the possibility of a complex formation through donating an electron from a non-bonding molecular orbital in a Lewis base to a vacant π-orbital of an acceptor (n → π) interaction with resonance stabilization of the combination (Mulliken, 1950; 1952; 1952). Many compounds like multirings aromatic hydrocarbons, aromatic amines form charge transfer complex with many acceptors (Srivastave et al., 1966; 1970; Dwinedi et al.,1983). Charge transfer interactions formed between perhydrosoquinoline as donor with 2,6-dichloroquinone-4- chloroimide, 2,6-dichromoquinone-4-chloroimide, chloranilic acid and picric acid as acceptors have been studied spectrophotometrically (Refat et al., 2008). Conductometric study for formation of charge transfer complexes, revealed that the stoichiometry of naphthalene- picric acid complex as 1:1 and that of the biphenyl-picric acid and p-phenylene-diamine: p-chloranil complexes as 2:1 (Ramanamurti et al.,1982). A spectrophotometric method is developed for the quantitative determination of some primary aliphatic and aromatic amines, based on the interaction between these amines and 2,4-dinitrofluorobenzene (Al-Sabha et al.,2015). The spectrophotometric characteristics of the solid charge-transfer molecular complexes (CT) formed in the reaction of the electron donor 2-amino-6-ethylpyridine with the π-acceptors have been studied. The results show that the formed solid CT complexes have ratio 1:2 with tetracyanoethylene and 2:1 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Mostafa et al., 2014). Energy minimization is an important step in molecular modeling with applications in molecular docking and in mapping binding sites. Charge transfer complexes of substituted aryl Schiff bases as donors with picric acid and m-dinitrobenzene as acceptors were investigated by using computational analysis calculated (Al-Harbi et al.,2014). The reaction of 2,3-dichloro-1,4-naphthoquinone with crizotinib was investigated, the stoichiometric ratio was found to be 2:1. Computational molecular modeling for the complex was conducted and the mechanism of the reaction was postulated (Alzoman et al., 2015). Spectroscopic and computational studies on the CT complex of 1,10-
phenanthroline and picric acid have been studied with a view to know the type and nature of interaction between them (Srivastavaa et al., 2015).

In this work, we synthesize some new charge transfer complexes of benzochromene (BC) as an electron donor with picric acid (PA), chloranilic acid (CLA) and 2,3-dichloro-1,4-naphthquinone (DNQ) as π-acceptors (Formula 1). UV-V and IR spectroscopic studies of compounds are used to deduce the structure and new electrical behavior of these new compounds. Calculations of the formation constant \( K_{fT} \), molar extinction coefficient \( (ε_{CT}) \), standard free energy \( (ΔG^o) \), oscillator strength \( (f) \) and transition dipole moment \( (μ) \) also the HOMO-LUMO energy gap of the molecules have been done.

![Formula 1](image)

**Experimental:-**

1. **Materials:-**

All chemicals used were of analytical grade. Benzochromene was prepared as reported elsewhere (Barsy et al., 2015) and purity of the obtained product was checked by melting point and elemental analysis measurements [\( C_{22}H_{10} NO_3 \); Mol. wt. = 345.398; white; M.p. = 220 °C; Calc.: % C 44.53, % H 2.39; Found: % C 42.99, % H 2.89]. Picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone were purchased from Sigma.

2. **Physical measurements:-**

The electronic absorption spectra were recorded in the region of 800–200 nm by using a Perkin-Elmer Lambda 25 spectrophotometer with a 1 cm quartz cell. The mid infrared spectra (IR) measurements of the solid CT-complexes as KBr discs were carried out on a Genesis II FTIR spectrophotometer in the range of 4000–400 cm\(^{-1}\). Melting point was measured on Gallenkamp melting point apparatus and is uncorrected. The data of the elemental analyses of the newly synthesized CT-complexes are consistent with the molar ratio results obtained from the photometric titrations.

3. **Photometric titrations:-**

The reported photometric titrations were performed at different wavelengths namely 351, 294 and 408 nm for the complex derived from benzochromene and picric acid (complex I), chloranilic acid (complex II) and 2,3-dichloro-1,4-naphthquinone (complex III) respectively. A 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 or 3.00 ml aliquot of a standard solution (5.0 × 10\(^{-4}\) mol/L) of the appropriate acceptors in methanol was added to 1.00 ml of 5.0×10\(^{-4}\) mol/L of donor also in methanol. The total volume of the mixture was made up to 5 ml. The concentration of donor \( (C_D) \) in the reaction mixture was thus fixed at 1.0×10\(^{-3}\) mol/L while the concentration of π-acceptors \( (C_A) \) varied from 0.25×10\(^{-3}\) to 3.00×10\(^{-3}\) mol/L. These concentrations produce donor: acceptor ratios from 4:1 to 1:4. The absorbance of each CT complexes was measured and plotted as a function with the ratio of \( (C_D):(C_A) \) according to a known method (Skoog, 1985). Modified Benesi–Hildebrand plots were constructed to allow the calculation of the formation constant, \( K_{fT} \), and the molar extinction coefficient, \( ε_{CT} \), values for each CT complex in this work (El-Kourashy, 1981).

4. **Syntheses Solid Charge Transfer Complexes:-**

The solid CT-complexes were prepared by mixing 1 mmole of the Benzochromene in methanol (20 ml) with 2 mmole of picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone in the same solvent (10 ml). The mixtures were stirred at room temperature for 3 h then left over night to separate the solid complex I, II and III respectively which were filtered off, washed several times with little amounts of methanol, and then dried under vacuum over anhydrous calcium chloride (Formula 2). The complexes were characterized using spectroscopic techniques (IR and UV-vis) and elemental analysis in addition to some physical properties and the results are summarized as follows:

**Complex I:** \( C_{18}H_{12}N_4O_7 \); Calc.: % C = 50.842; % H = 3.137; Found: % C = 50.99; % H = 3.79; Mol.wt. = 803.33; M.p.= 285°C; yellow.

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Complex II: C_{34}H_{23}NCl_4O_11; Calc.: %C=53.52; %H=3.04; Found: %C = 53.37; %H, 3.09; Mol. wt. = 762.98; M.p. = 290°C; Dark brown.
Complex III: C_{42}H_{27}NCl_4O_7; Calc.: % C = 63.13; % H = 3.41; Found: % C = 63.71; %H = 3.12; Mol. wt. = 799.10; M.p. = 270°C; yellow.

5. Computational studies:-
The drawing of the structure of the donor and acceptors were carried out on the Chem. Draw ultra 12.0 software and for optimization the obtained structures were transported to program Chem. 3D ultra 12.0.

Results and Discussion:-
1. Infrared Spectra:-
The peak assignments for the important characteristic IR spectral bands for the formed CT complexes are shown in Figure 1 and Table 1. A comparison of the relevant IR spectral bands of the free benzochromene (BC) and the studied acceptors (PA, CLA and DNQ) with the corresponding bands in the IR spectra of the isolated solid CT complexes clearly indicated that the characteristic bands of the BC exhibit small shifts in frequency and changes in their band intensities (νOH, νNH at 3403-2903 cm\(^{-1}\) and νC=O at 1525 cm\(^{-1}\)). This result could be attributed to the expected changes in symmetry and electronic configurations upon the formation of the CT complexes.

The ν(OH) stretching vibrations in the free PA and CLA appeared at 3416, 3235 cm\(^{-1}\), respectively, where in the formed CT complexes, these stretching vibrations occurred at 3430 cm\(^{-1}\) for complex I; at 3481 cm\(^{-1}\) for complex II.

The IR spectrum of the complexes I, II are characterized by appearing of band at 3032, 3232 cm\(^{-1}\) which does not appear in the spectra of the free donor or PA and CLA. This band can be attributed to the stretching vibration of the intermolecular hydrogen bond (OH---N) in the complex formed through the transfer of a proton from the acidic center of PA and CLA to the donor as dictated by acid–base theory (Adam, 2012; 2013). The shift of the IR bands of the acceptor to lower wavenumbers reflects a donor to acceptor charge transfer of n → π* interaction, D\(^{HOMO}\) → D\(^{LUMO}\) transition (Formula 2) (Bharathikannan et al., 2008).

In the complex III, the stretching vibration of ν(C=O) appear at 1621 cm\(^{-1}\) was shifted to a lower value 1587 cm\(^{-1}\), that is indicative of the involvement of the (C=O) group in the CT-complexation. The π→π* CT complex III is formed via the benzochromene (electron-rich group) and the DNQ (electron acceptor). The chloro- and C=O are an electron withdrawing groups that exists in DNQ. The chloro and C=O groups in DNQ withdraw electrons from the aromatic ring and such a process will make the aromatic ring an electron accepting region (Formula 2). It might also to indicate here that ν(NO\(_2\)) vibrations of PA show some changes particularly in terms of band wavenumber values from 1861 to 1813 cm\(^{-1}\) upon complexation. The stretching vibration of ν(C-Cl) appears at 981 and 851 cm\(^{-1}\) for CLA; at 889 and 838 cm\(^{-1}\) for DNQ. This band is observed at a range of 823-978 cm\(^{-1}\) for the CT complexes II and III.
Fig. 1. IR data for donor, I, II and III CT complexes.

Formula 2. Suggested structure of I [BC(PA)₂], II [BC(CLA)₂] and III [BC(DNQ)₂] complexes.

Table 1. Electronic (nm), IR (cm⁻¹) data for the new CT complexes.

| Compound          | λₘₚₙ, nm | v O-H + uN-H | OH--N | uC=O       |
|-------------------|----------|--------------|-------|------------|
| Complex I [BC(PA)₂] | 210, 216, 225, 234, 355 | 3485, 3352 | 3032  |            |
| Complex II [BC(CLA)₂] | 228, 254, 275, 302, 307, 311, 524 | 3485      | 3232  | 1541       |
| Complex III [BC(DNQ)₂] | 214, 220, 230, 236, 240, 244, 260, 288, 336 | 3404      | -     | 1587       |

2. Electronic absorption spectra:-

The electronic absorption spectra of the Benzochromene, π-acceptors and the resultant charge transfer complexes are shown in Fig. 2. The spectra revealed new strong absorption bands assigned to the CT interaction at 355, 524 and 336 nm for I, II and III complexes, respectively (Table 1). The photometric titration (Skoog, 1985) measurements between benzochromene and CLA, DNQ and PA in methanol based on the characteristic absorption bands with reference to the CT-complexes (Fig. 3), proved that the molar ratio of the resultant complexes is 1:2 donor:acceptor (Fig. 4). It was necessary to calculate the values of the formation constant (Kₐ₅�) and the extinction coefficient (εₐ₆ₐ) of the complexes. For this purpose, the 1:2 modified Benesi–Hildebrand equation was used in the calculations (El-Kourashy, 1981):

\[(Ca)^2C_d/A = 1/K_{CT}ε_{CT} + 1/ε_{CT} C_a (4C_d + C_a)\]

where Cₐ and C₃ are the initial concentration of the acceptors and donor, respectively and A is the absorbance of the detected CT band. The data obtained Cₐ, C₃, (Ca)²C₃, Cₐ(4C₃+Cₐ) and (Ca)²C₃/A were calculated. By plotting (Ca)²C₃/A values vs. Cₐ(4C₃+Cₐ), straight lines are obtained with a slope of 1/εₐ₆ₐ and an intercept of 1/Kₐ₆ₐCT.
The values of both $K_{CT}$ and $\varepsilon_{CT}$ associated with these complexes are given in Table 2. The data resulted (Table 2) show that the complexes give high values of both formation constant ($K_{CT}$) and molar extinction coefficient ($\varepsilon_{CT}$). The high values of both $K_{CT}$ and $\varepsilon_{CT}$ of the resultant CT-complexes caused high stabilities of the formed CT-complexes to be expected as a result of the expected high donation of the benzochromene.

![Fig. 2. Electronic absorption spectra of the donor, acceptors and of the CT-complexes I, II and III. The blue color is for the donor and the black color is for the acceptors while the orange color is for the CT complexes.](image1)

![Fig. 3. Photometric titration curves of picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthquinone with benzochromene.](image2)

![Fig. 4. The plot of Ca(4Cd + Ca) values against (Ca)$^2$Cd/A values of I, II and III complexes.](image3)

3. Physicochemical parameters for the charge transfer complexes:-

In order to characterize the formation of the complexes between BC and the acceptors, some physicochemical parameters were estimated to explain the propensity of the formation of the complexes. The oscillator strength (f) is a dimensionless quantity used to express the transition probability of the CT band. The oscillator strength (f) was obtained from the approximate formula (Tsubomura et al., 1964):

$$f = 4.319 \times 10^{-9} \varepsilon_{CT} \nu$$
The transition dipole moment ($\mu$) of the CT complex calculated from equation (Rathore et al., 1997):

$$\mu (\text{Debye}) = 0.0958 \left[ \varepsilon_{CT} \nu_{CT}/\nu_{CT} \right]^{1/2}$$

where $\Delta\nu_{CT}$ is the half-width, that is the width of the band at the half the maximum absorption, and $\Delta\nu$ is the wavenumber at the absorption maximum.

The resonance energy of the complex ($R_N$) in the ground state is obtained from the theoretical equation derived by Brieglab (Briegleb et al., 1960):

$$\varepsilon_{CT} = 7.7 \times 10^{-4}/[h\nu_{CT}/[R_N]-3.5]$$

where $\varepsilon_{CT}$ is the molar absorptivity of the complex at the maximum of the CT absorption, $h\nu_{CT}$ is the transition energy of the complex.

The transition energy ($E_{CT}$) of the complex which is obtained from the expression (Briegleb et al., 1964):

$$E_{CT} = h\nu_{CT} (\text{eV}) = 1243.667/R_{CT}(\text{nm})$$

where $h$ is Planck’s constant, $\nu_{CT}$ is the wavenumber of the absorption peak of the CT complex and $\lambda_{CT}$ is the wavelength of the characteristic complexation band. The calculated spectroscopic and physical values ($f$, $\mu$, $R_N$ and $E_{CT}$) for the CT complexes using these equations are presented in Table 2.

In Table 2, the values of ionization potential of donor in CT complexes $I$, $II$ and $III$ are known. Assuming $I$ for 4-aminoethyl) phenol and the associated values of $\nu_{CT}$ are known. Assuming $I$ for 4-(2-aminoethyl) phenol - picric acid complex = 9.64 eV and $\nu_{CT} = 3.16$ eV (AbuYamin et al., 2013), we have estimated the value of ionization potential of donor = 9.993(eV). The average value of ionization potential of donor estimated by three different methods =10.058 (eV).

There is a little difference between the three sets of values.

From the above equation, the value of ionization potential of donor with picric acid in CT of complex $I$ = 10.08 (eV).

The transition dipole moment ($\mu$) of the CT complex calculated from equation (Rathore et al., 1997):

$$\mu (\text{Debye}) = 0.0958 \left[ \varepsilon_{CT} \nu_{CT}/\nu_{CT} \right]^{1/2}$$

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$$E_{CT} = h\nu_{CT} (\text{eV}) = 1243.667/R_{CT}(\text{nm})$$

where $h$ is Planck’s constant, $\nu_{CT}$ is the wavenumber of the absorption peak of the CT complex and $\lambda_{CT}$ is the wavelength of the characteristic complexation band. The calculated spectroscopic and physical values ($f$, $\mu$, $R_N$ and $E_{CT}$) for the CT complexes using these equations are presented in Table 2.

In Table 2, the values of ionization potential of donor in CT complexes $I$, $II$ and $III$ are known. Assuming $I$ for 4-aminoethyl) phenol and the associated values of $\nu_{CT}$ are known. Assuming $I$ for 4-(2-aminoethyl) phenol - picric acid complex = 9.64 eV and $\nu_{CT} = 3.16$ eV (AbuYamin et al., 2013), we have estimated the value of ionization potential of donor = 9.993(eV). The average value of ionization potential of donor estimated by three different methods =10.058 (eV).

There is a little difference between the three sets of values.

The ionization potential of the donor in the charge transfer complex is calculated using the empirical equation derived by Aloisi and Pigantro (Aloisi et al., 1972).

$$I_p (eV) = 5.76 + 1.53 \times 10^{-4} \nu_{CT}$$

From the above equation, the value of ionization potential of donor with picric acid in CT of complex $I$ = 10.08 (eV).

The ionization potential of an unknown donor can be obtained from the $h\nu_{CT}$ vs Ip plot (Ghosh et al., 1993) for PA with a number of other donors, hexol (Refat et al., 2013), p-nitroaniline (Singh et al., 2009), ibuprofen (Sultana et al., 2013), N-dimethylbenzylidene aniline (Gaber et al., 1988). Evaluated Ip values of benzochromene are shown in the inset, provided the value of $\nu_{CT}$ for the unknown donor is known for the same acceptor, the value of Ip obtained from this plot for donor =10.1 eV (figure 5). The charge-transfer band energy can be approximately related to the ionization potential of the donor and electron affinity of the acceptor molecule given by equation (Foster et al., 1966),

$$h\nu_{CT} = Ip - E_A - W$$

where $h$ is the Planck's constant, $\nu_{CT}$ is the frequency corresponding to the lowest energy intermolecular charge-transfer band, $Ip$ is the ionization potential of the donor, $E_A$ is the electron affinity of the acceptor and $W$ is a constant.

Again assuming that the dissociation energy $W$ values are essentially constant for similar type of complexes, the relationship between the ionization potential of two donors and the values of $\nu_{CT}$ with a common acceptor (PA) can be written as:

$$Ip\text{ donor (2)} = Ip\text{ donor (1)} + h\nu_{CT}(2) - h\nu_{CT}(1).$$

From the above, the value of ionization potential of donor (2) can be estimated if the ionization potential of donor (1) and the associated values of $\nu_{CT}$ are known. Assuming $Ip$ for 4-(2-aminoethyl) phenol - picric acid complex = 9.64 eV and $\nu_{CT} = 3.16$ eV (AbuYamin et al., 2013), we have estimated the value of ionization potential of donor = 9.993(eV). The average value of ionization potential of donor estimated by three different methods =10.058 (eV).

There is a little difference between the three sets of values.

In Table 2, the values of ionization potential of donor in CT complexes $I$, $II$ and $III$ by using equation derived by Aloisi and Pigantro. The dissociation energy ($W$) of the formed CT complex between donor and acceptors was calculated from the transition energy ($h\nu_{CT}$), ionization potential of the donor ($Ip$) and the electron affinity of picric acid ($E_A = 1.1$). The dissociation energy was found to be 2.651 (eV).
Fig. 5. Plot of $h\nu_{CT}$ against $I_p$ for CT complexes of picric acid with 1-hexol, 2-p-nitroaniline, 3-Ibuprofen and 4-N-dimethylbenzylidene aniline.

Table 2. Physicochemical parameters of the CT complexes

| Complex          | $\lambda_{CT}$ (nm) | $K_{CT}$ (Lmol$^{-1}$) | $\varepsilon_{CT}$ (Lmol$^{-1}$cm$^{-1}$) | $F$ | $\mu$ | $R_N$ (eV) | $I_p$ | $\Delta G$ (KJ mol$^{-1}$) | $E_{CT}$ (eV) |
|------------------|---------------------|------------------------|------------------------------------------|-----|-------|----------|-------|-------------------------|--------------|
| [BC(PA)$_2$]     | 354                 | 2.351x10$^6$           | 10.702x10$^6$                           | 4.97 | 19.36 | 0.36     | 10.08 | 36.346                 | 3.513        |
| [BC(CLA)$_2$]    | 524                 | 12.784x10$^6$          | 5.470x10$^6$                            | 1.55 | 13.63 | 0.119    | 8.680 | 40.542                 | 2.373        |
| [BC(DNQ)$_2$]    | 336                 | 13.252x10$^6$          | 24.563x10$^6$                           | 21.49 | 40.017| 0.857    | 10.314| 47.884                 | 3.701        |

4. Molecular Modeling and energy gap:

For investigating the site of interaction and postulate the reaction mechanism, modeling for the CT complex was performed. It was found that the highest electron density in the benzochromene molecule is located on the nitrogen atom of the amino group. The total charge on the nitrogen atom was found to be -0.103, the negative sign indicate the negative electron density. As well, it was found that acceptors moves toward the NH$_2$ group of donor to form the CT complex (Figure 6). In the NH$_2$ group, nitrogen can donate a major share of the lone pair of electrons to the oxygen atom of picric acid and chloranilic acid. This leads to the development of partial negative charges on the oxygen atom and this makes them capable of forming the charge transfer complex. Other centers did not contribute in the CT reaction based on the fact that certain electron density was required for achievement of a successful electron transfer (Foster, 1969).

The HOMO-LUMO energy gap of donor, acceptors and CT complexes were calculated (Table 3). It is known that the value of $E_{\text{HOMO}}$ is often associated with the electron donating ability of inhibitor molecule, higher values of $E_{\text{HOMO}}$ is an indication of the greater ease of donating electrons to the unoccupied orbital of the acceptor. The value of $E_{\text{LUMO}}$ is related to the ability of the molecule to accept electrons, lower values of $E_{\text{LUMO}}$ shows the acceptor would accept electrons. Consequently, the value of Egap provides a measure for the stability of the formed complex.

The order of stability can be summarized as: I > II > III. In the Fig. 6, show that acceptors are perpendicular to the molecular plane of donor. The optimized bond length, bond angle and dihedral angles of complexes which are calculated.

Table 3: The HOMO-LUMO energy gap of donor, acceptors and CT complexes in eV.

| Compound                                    | HOMO  | LUMO  | Energy gap |
|---------------------------------------------|-------|-------|------------|
| Benzochromene (BC)                          | 0.236 | 1.53  | -1.294     |
| Picric acid (PA)                            | -11.290| -6.221| -5.069     |
| Chloranilic acid (CLA)                      | -8.885| -7.326| 1.559      |
| 2,3-dichloro-1,4-naphthquinone (DNQ)        | -9.697| -7.195| -2.502     |
| Complex I [BC(PA)$_2$]                      | -6.523| -5.580| -0.943     |
| complex II [BC(CLA)$_2$]                    | -8.021| -6.935| -1.086     |
| complex III [BC(DNQ)$_2$]                   | -9.956| -7.997| -1.959     |
Fig 6. Picture of HOMO-LUMO of donor, acceptors and CT complexes.

|                           | HOMO       | LUMO       |
|---------------------------|------------|------------|
| **Benzochromene (BC)**    | ![Image](image1) | ![Image](image2) |
| **Picric acid (PA)**      | ![Image](image3) | ![Image](image4) |
| **Chloranilic acid (CLA)**| ![Image](image5) | ![Image](image6) |
| **2,3-dichloro-1,4-naphthquinone (DNQ)** | ![Image](image7) | ![Image](image8) |
**Conclusions:**
The CT reaction of benzochromene as electron donor and picric acid, chloranilic acid and 2,3-dichloro-1,4-naphthoquinone as electron acceptors has been investigated. The obtained complexes were studied by spectrophotometric method. The formation constant ($K_{CT}$), the molar extinction coefficient ($\varepsilon_{CT}$) and physicochemical parameters ($f, \mu, R_N, I_p, \Delta G$ and $E_{CT}$) for the CT complexes were calculated. The HOMO-LUMO energy gap of the donor, acceptors and CT complexes has been obtained.

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