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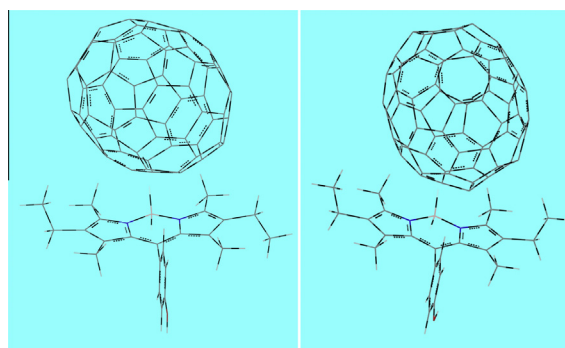
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journal homepage: www.elsevier.com/locate/saaCharge transfer in the electron donor–acceptor complexes of a *meso*-phenol BODIPY dye with chloranils and fullerenesAnimesh Karmakar^a, Tandrima Chaudhuri^{a,*}, Soumyaditya Mula^b, Subrata Chattopadhyay^b^a Department of Chemistry, Dr. Bhupendranath Dutta Smriti Mahavidyalaya, Burdwan 713 407, India^b Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

HIGHLIGHTS

- Vertical IP of *meso*-phenol analogues of PM567 dye (**1c**) in toluene medium.
- Lower energy shifting of CT band with decreasing EA of the electron acceptors.
- The degree of the CT transition increases with increasing EA of acceptors.
- **1c** having higher IP than PM567 (**1a**), both are good electron donor.
- Comparative analysis of PM567 (**1a**), its *meso*-phenyl (**1b**) and *meso*-phenol (**1c**) analogues.

GRAPHICAL ABSTRACT

[70]fullerene can approach **1c** both horizontally and vertically.

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ABSTRACT

UV–Vis spectral investigations of electron donor–acceptor complexes of laser dye 2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4'-hydroxyphenyl)-4-bora-3a,4a-diaza-s-indecene (**1c**) with chloranils and fullerenes are reported in toluene medium. Well defined charge transfer (CT) absorption bands have been located in the visible region. Oscillator strengths, transition dipole and resonance energies of the CT complexes have been estimated. Vertical ionization potential of **1c** has been determined utilizing Mulliken's equation. A possible mechanism for the interaction between electronic subsystems of chloranils, [60]- and [70]fullerenes with three different BODIPY dyes (**1a**, **1b** and **1c** shown in Fig. 1) have been discussed in comparing the parameters like degree of charge transfer and binding constant in nonpolar toluene. Comparison of **1c** complexes is done with DFT/B3LYP/6-31G optimized gas phase geometries.

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Introduction

Through proper designing electron deficient BODIPY chromophore can behave as efficient fluorescent sensor that can form exciplexes with different metal ions in aqueous medium [1] or in acetonitrile [2] solutions. BODIPY dyes have been also widely

applied as fluorescent sensors and probes to study biological systems containing lipids, nucleic acids or proteins [3–5], as well as light harvesting arrays to develop antenna systems [6–9]. In our previous study it was found that solvatochromic BODIPY (**1b**) dye [10] can recognize fullerenes selectively [11]. Versatile BODIPY dye is inherently electron deficient due to the presence of tetravalent boron and therefore it is expected that charge transfer interaction can take place in presence of good electron donor. However, **1a** dye

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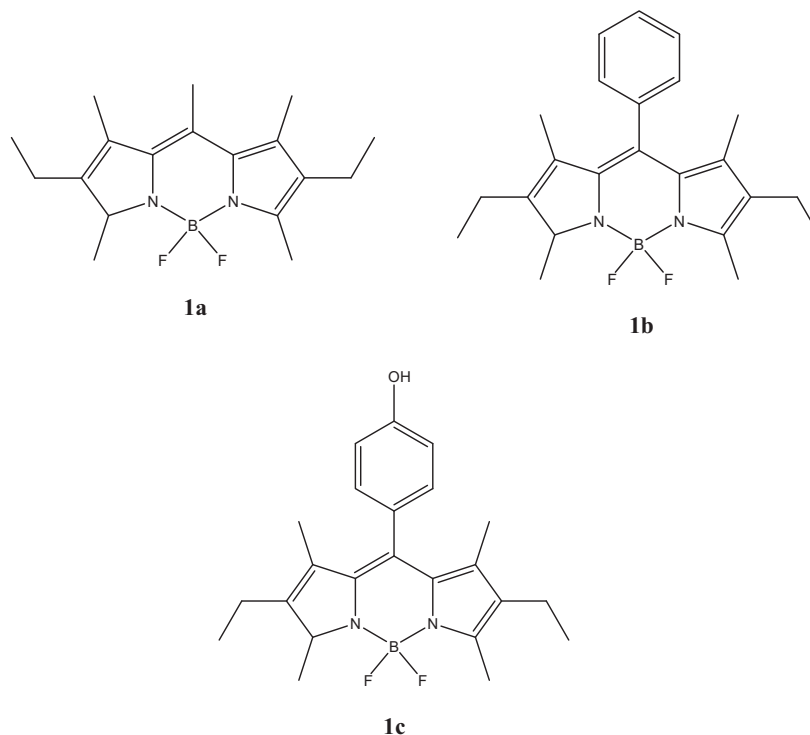


Fig. 1. Structure of the BODIPY dyes **1a**, **1b** and **1c**.

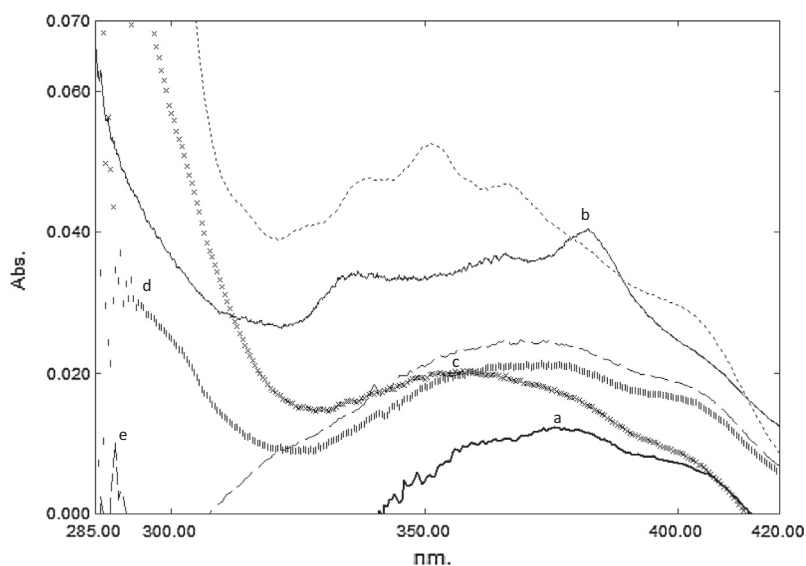


Fig. 2. CT absorption spectra of (a) [60]fullerene (1.39×10^{-5}) + **1c** ($4.035 \times 10^{-6} \text{ mol dm}^{-3}$); (b) [70]fullerene ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$) + **1c** ($4.035 \times 10^{-6} \text{ mol dm}^{-3}$); (c) DDQ ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$) + **1c** ($4.035 \times 10^{-6} \text{ mol dm}^{-3}$) plotted along with the pristine acceptor solution as reference and (d) absorption spectra of only **1c** plotted along with the solvent as reference.

is found to show stable charge transfer band with well known electron acceptors in the visible region [12].

We have taken this opportunity to compare the nature of interactions between fullerenes and chloranils with **1a**, **1b** and **1c** for explaining the electronic subsystems of the three BODIPY dye molecules, hence, widens the scope of the present investigation on molecular interactions of fullerenes and chloranils with various other dye molecules.

Experimental

[60]- and [70]Fullerenes have been purchased from Merck, Germany and Aldrich, USA respectively. *o*-chloranil is collected from Aldrich, USA. *p*-chloranil has been obtained from Fluka, Lausanne, Switzerland, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) from Sigma. BODIPY dye 2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4'-hydroxyphenyl)-4-bora-3a,4a-diaza-s-indecene (**1c** in

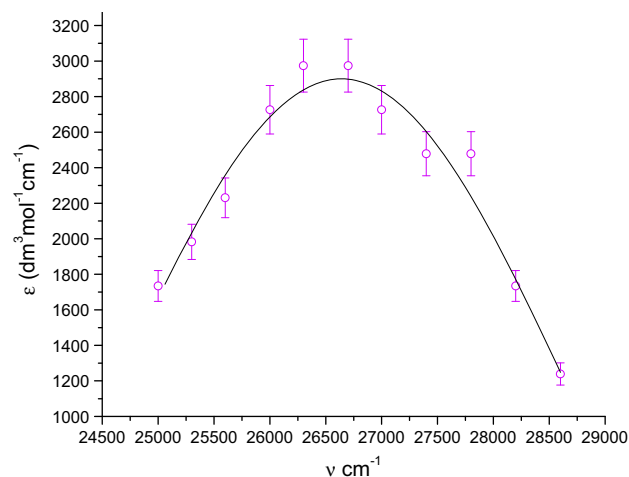


Fig. 3. Gaussian curve analysis of the shoulder region of the CT band for [60]fullerene/1c system.

Fig. 1) has been synthesized by our reported method [13]. The solvent, toluene, is of HPLC grade (Merck) and is used without further purification. UV–Vis absorption spectra are recorded on a Shimadzu UV 1800 spectrophotometer. Theoretical calculations have been performed in DFT/B3LYP level in 6-31G basis set (Gaussian'09).

Results and discussion

Observation of CT bands

Fig. 2 shows the electronic absorption spectra of mixtures containing (1c + [60]fullerene), (1c + [70]fullerene) and (1c + DDQ) in toluene medium. To obtain the CT bands, spectra of above solution (in toluene medium) are recorded against the pristine acceptor solution as reference to cancel out the acceptor absorbance. It is observed that new absorption peaks appear in the visible region. Similar spectral features have been obtained with mixtures containing (1c + *o*-chloranil) and (1c + *p*-chloranil) also. The CT absorption spectra were characterized by fitting to the gaussian function

$$y = y_0 + \left[\frac{A}{\left(w \sqrt{\pi/2} \exp[-2(x - x_c)^2/w^2] \right)} \right] \quad (1)$$

where x and y denote wavenumber and molar extinction coefficient respectively. When such a Gaussian fit (approximated by the above approximation) is applied over a wide range of (x, y) data points, y_0 obviously represents the lowest bound within the y -values in the range and the remaining term in the expression represents a positive definite quantity. At the value of $x = x_c$, the derivative dy/dx disappears giving $y_c = y_0 + A/\{w\sqrt{\pi/2}\}$ which bears a numerical significance at the band centre in respect of the plot. However, as $x \rightarrow \infty$, $y \rightarrow y_0$ which implies a significance to hypothetical absorbance value in the limit of infinite wavelength assuming that the data is included

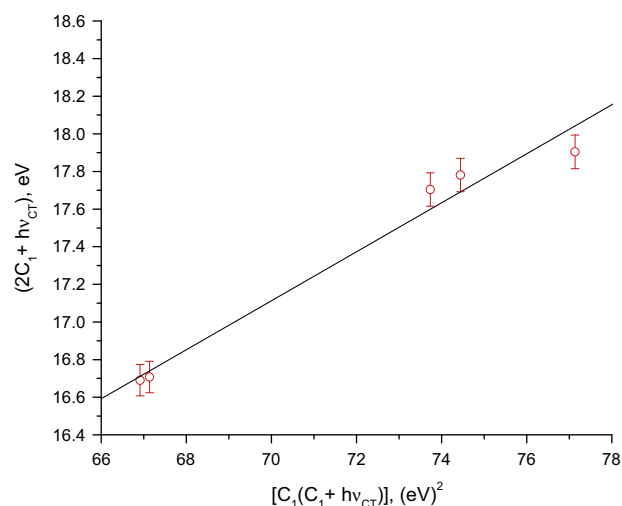


Fig. 4. Plot of $(2C_1 + hv_{CT})$ eV vs. $C_1(C_1 + hv_{CT})$ (eV)² for the CT complexes of 1c.

within the range. One such plot is shown in Fig. 3. The results of the Gaussian analysis for all the 1c – acceptor systems under study are shown in Table 1. The wavelengths at these new absorption maxima ($\lambda_{max} = x_c$) and the corresponding transition energies ($h\nu$) are summarized in Table 1. The gaussian analysis fitting is done in accordance with the method developed by Gould et al. [14]. One important point to mention here is that Gaussian analysis of a curve generally gives a decent result near the maxima of the curve spread over a very small region. For this reason, although the errors in the center of the CT spectra for the complexes of 1c with various electron acceptors are very small, there are appreciable errors in the y_0 value. Even though fullerenes and 1c undergo CT interaction with great ease, one can still argue that the way they approach to each other is dictated by packing consideration than by the special affinity we highlight above. For this reason, we have investigated the attraction of [60]- and [70]fullerenes to 1c in a nonpolar solvent like toluene. Toluene is chosen as solvent primarily to obtain practical levels of solubility but it serves another important purpose. As an excellent solvent for both fullerenes and 1c, any fullerene/1c attraction must compete with 1c/toluene interactions. The choice of a nonpolar solvent undoubtedly promotes the aggregation of the hydrophobic fullerene and 1c entities but this may be viewed as natural enhancement of their affinity. The demonstration of fullerene/1c binding in toluene is therefore considered a particularly stringent test of the spontaneous attraction.

Determination of vertical ionization potential (I_D^v) of 1c

For complexes with neutral ground state, a CT band corresponds to a transfer of an electron from a donor to an acceptor molecule with the absorption of a quantum:

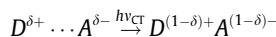


Table 1

Gaussian curve analysis for the CT spectra of 1c *o*-chloranil, *p*-chloranil, DDQ, [60] and [70]-fullerenes in toluene.

System	Area under curve (A) $\times 10^{-7}$ (dm ³ mol ⁻¹)	Width of the curve (w) (cm ⁻¹)	Center of the curve (x_c) (cm ⁻¹)	y_0 (dm ³ mol ⁻¹ cm ⁻¹)
1c/C ₆₀	2.4121 \pm 0.3018	4166.0 \pm 2010.0	26,641 \pm 34.92	–1720.3 \pm 360.1
1c/C ₇₀	0.9222 \pm 0.3527	1353.4 \pm 197.97	26,256 \pm 3.90	4534.7 \pm 1301.4
1c/DDQ	0.1797 \pm 0.0219	1547.7 \pm 100.25	27,951 \pm 13.40	4092.2 \pm 61.3
1c/ <i>p</i> -chloranil	0.6839 \pm 0.2109	1478.5 \pm 354.39	34,672 \pm 126.4	5200.42 \pm 414.76
1c/ <i>o</i> -chloranil	1.8474 \pm 0.0600	128.1 \pm 1.53	34,565 \pm 2.40	–131.53 \pm 6.18

Table 2

CT absorption maxima and transition energies of the complexes of **1c** with *o*-chloranil, *p*-chloranil, DDQ, [60] and [70]-fullerenes and the reported values of **1a**^a in toluene.

Parameters	C ₆₀	C ₇₀	DDQ	<i>p</i> -Chloranil	<i>o</i> -Chloranil
1c					
λ_{CT} (nm)	375.51	380.95	357.60	288.37	289.16
$h\nu_{CT}$ (eV)	3.30	3.26	3.47	4.30	4.29
f (dm ³ mol ⁻¹ cm ⁻²)	0.1042	0.0398	0.0078	0.0295	0.0798
R_N (eV)	0.1638	0.1843	0.04	0.1765	1.0283
μ_{EN} (D)	7.2439	7.8584	3.2439	6.4747	36.1529
$\alpha \times 10^3$	8.86	8.85	8.94	8.95	9.05
$K_{BH} \times 10^{-4}$	2.12	3.93	0.7044	2.58	5.55
I_D^v (eV)			7.6764		
1a ^a					
λ_{CT} (nm)	393.5	460.4	419.7	471.3	418.7
$h\nu_{CT}$ (eV)	2.87	2.45	2.69	2.39	2.69
f (dm ³ mol ⁻¹ cm ⁻²)	0.415	7.670	0.110	0.0017	0.015
R_N (eV)	0.1195	0.5512	0.0358	0.0059	0.0050
μ_{EN} (D)	6.26 ^b	50.20 ^b	4.23 ^b	0.46 ^b	1.42 ^b
$\alpha \times 10^3$	5.30 ^b	6.04 ^b	5.18 ^b	5.19 ^b	5.20 ^b
$K_{BH} \times 10^{-4}$	0.1180	0.027		–	
I_D^v (eV)			7.4500		

^a Reported in Ref. [12].

^b Calculated from data of Ref. [12].

The relationship between the energy ($h\nu_{CT}$) of the lowest energy intermolecular CT band and the I_D^v of the donor for a series of complexes with a common donor species has been the source of much discussion. According to Mulliken's theory [15] the ground state of the complex is a resonance hybrid of a 'no – bond' state ($D \cdots A$) and a dative state (D^+A^-) with the former predominating; the excited state is a resonance hybrid of the same two structures with the dative one predominating. CT transition energies in these complexes are related to the vertical ionization potentials (I_D^v) of the donors by the relation,

$$h\nu_{CT} = (I_D^v - C_1) + C_2 / (I_D^v - C_1) \quad (2)$$

$$\text{Here } C_1 = E_A^v + G_1 + G_0 \quad (3)$$

where E_A^v is the vertical electron affinity of the acceptor, G_0 is the sum of several energy terms (like dipole – dipole, van der Waals interaction, etc.) in the 'no – bond' state and G_1 is the sum of a number of energy terms in the 'dative' state. In most cases G_0 is small and can be neglected while G_1 is largely the electrostatic energy of attraction between D^+ and A^- . The term C_2 in Eq. (2) is related

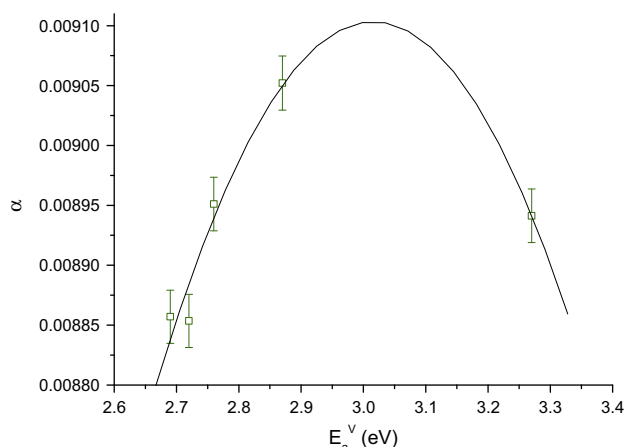


Fig. 5. Degree of charge transfer vs. electron affinity.

to the resonance energy of interaction between the 'no – bond' and 'dative' forms in the ground and excited states and for a given donor it may be supposed to be constant [15]. A rearrangement of Eq. (2) yields

$$2C_1 + h\nu_{CT} = [C_1(C_1 + h\nu_{CT})/I_D^v] + (C_2/I_D^v) + I_D^v \quad (4)$$

The vertical electron affinities of [60]fullerene, [70]fullerene, *p*-chloranil, DDQ and *o*-chloranil were collected from references [16–19]. G_0 is neglected and except [60]- and [70]fullerenes, the typical D–A distance in π -type EDA complexes to be 3.68 Å. The D–A distance in [60]- and [70]fullerenes are more or less similar and is 3.61 Å (using DFT optimized geometries). Using these values, the major part of G_1 is estimated for different acceptors and thus C_1 is obtained from Eq. (3) for each of the acceptors. A plot of $2C_1 + h\nu_{CT}$ vs. $C_1(C_1 + h\nu_{CT})$ for a given donor and various acceptors yields a slope of $1/I_D^v$ from which the value of I_D^v has been estimated as 7.68 eV for **1c**. The following linear regression equation has been obtained with the present data:

$$2C_1 + h\nu_{CT} = (0.1303 \pm 0.0121)[C_1(C_1 + h\nu_{CT})] + (7.9940 \pm 0.8658); \text{ corrln. coeff.} = 0.99 \quad (5)$$

The above plot is demonstrated in Fig. 4. It should be noted that reorganization energies for different electron transfer (ET) reactions of covalent and electrostatic donor/acceptor complexes are primarily associated with solvent reorganization. The above feature can be formulated by applying Marcus theory of bimolecular ET [20]. The bimolecular ET reaction depends implicitly on the reactants, assuming inter nuclear configuration appropriate for the ET event to take place. In most bimolecular reaction it is assumed that ET at distances larger than contact is negligible, and therefore evaluation of K_{Act} reduces to a fixed distance problem at $r = \sigma$ (where σ is the sum of the reactant's radii, i.e., the contact distance). For our present systems DFT calculations compute dipole moments for [60]fullerene/**1c** and [70]fullerene/**1c** complexes as 4.36D and 4.21D respectively. For this reason, the work associated with binding the neutral reactants together for the systems reported herein will be insignificant, and consequently ET at distances larger than $r = \sigma$ do not contribute to the overall complexation process.

Degree of charge transfer (α)

To discuss the degrees of charge transfer (α) for the **1c** and fullerenes CT complexes, we use Mulliken's two-state model [15]. According to this model, the ground (ψ_g) and excited (ψ_{ex}) state wave functions of the CT complexes are described by a linear combination of the dative $\psi(D^0, A^0)$ and ionic $\psi(D^+, A^-)$ states,

$$\psi_g = \{\sqrt{(1 - \alpha)}\}\psi(D^0, A^0) + (\sqrt{\alpha})\psi(D^+, A^-) \quad (6)$$

$$\psi_{ex} = \{\sqrt{(1 - \alpha)}\}\psi(D^+, A^-) + (\sqrt{\alpha})\psi(D^0, A^0) \quad (7)$$

where $\psi(D^+, A^-)$ differs from $\psi(D^0, A^0)$ by the promotion of an electron from the donor to the acceptor molecule. In this model, α is expressed by

$$\alpha = (C_2/2) / [I_D^v - E_A^v + C_1]^2 + (C_2/2) \quad (8)$$

The values of α were calculated by using Eq. (8) and are given in Table 2. The values of α indicate that little extent of charge transfer takes place in the ground state. On an average with all the five acceptor molecules **1c** shows very weak charge transfer ability just

as was observed in case of **1a** [12]. The variation of degree of charge transfer with the electron affinities of the acceptors was shown in Fig. 5.

Table 2 indicates the reported [12] value of vertical ionization potential of **1a**, a well known BODIPY dye, to be 7.45 eV which is lower than that of **1c**. Thus for the same group of electron acceptors, **1c** requires higher energy to donate its outer electron compared to that of **1a**. However, **1c** contains phenolic OH group that has strong electron donating (+R) effect in place of methyl group (+I effect) of **1a**. Table 2 also indicates the values of degree of charge transfer (α) of these two BODIPY donors. On contrary to trend of ionization potential here in all cases **1c** is found to have higher degree of charge transfer compared to that of **1a**.

Determination of oscillator strength (f)

From the CT absorption spectra, we can estimate oscillator strength. The oscillator strength f is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \epsilon_{\text{CT}} d\nu \quad (9)$$

where $\int \epsilon_{\text{CT}} d\nu$ is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. The integral is to be formed from zero to infinity. To a first approximation

$$f = 4.32 \times 10^{-9} \epsilon_{\text{max}} \Delta\nu_{1/2} \quad (10)$$

where ϵ_{max} is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half-width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of the CT bands are summarized in Table 2 for both **1a** and **1c**.

Determination of transition dipole (μ_{EN})

The extinction coefficient is related to the transition dipole by

$$\mu_{\text{EN}} = 0.0952 [\epsilon_{\text{max}} \Delta\nu_{1/2} / \Delta\nu^{1/2}] \quad (11)$$

where $\Delta\nu \approx \dot{\nu}$ (wave number) at ϵ_{max} and μ_{EN} is defined mathematically as $-e \int \psi_{\text{ex}} \sum_i r_i \psi_g d\tau$. The μ_{EN} is the transition dipole moment for the transition between the neutral ground state and the excited state of the CT complex, r_i signifies the length of the position vector of the electron from the center of the coordinate axes and $d\tau$ is the volume element in three-dimensional coordinate space. The quantity e is the electronic charge. Values of μ_{EN} for the complexes of both **1a** and **1c** with five different electron acceptors are given in Table 2. The oscillator strength (f) is proportional to the square of transition dipole $|\mu_{\text{EN}}|^2$. The higher observed oscillator strength for the **1c**/[60]fullerene and **1c**/*o*-chloranil complexes in toluene as recorded in Table 2 might reflect the higher transition dipole when there is enough scope for the formation of stable π - π stacking and H-bonding interaction with [60]fullerene and *o*-chloranil respectively. In case of *o*-chloranil possibility of both π - π stacking and H-bonding interaction prevails.

Determination of resonance energy (R_N)

Briegleb and Czekalla [21] theoretically derived the relation

$$\epsilon_{\text{max}} = 7.7 \times 10^4 / [h\nu_{\text{CT}} / |R_N| - 3.5] \quad (12)$$

where ϵ_{max} is the molar extinction coefficient of the complex at the maximum of the CT absorption, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which, obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of R_N for the complexes under study have been given in Table 2. Trend in R_N value shows that *o*-chloranil forms most stable complex with **1c**

compared to other π -acceptors. [60]- and [70]fullerenes also form strong complexes with **1c**.

Determination of formation constants (K)

The formation constants of the **1c**/A complexes are determined using the Benesi-Hildebrand (BH) [22] equation in the form

$$-\frac{1}{d} = \frac{1}{\epsilon[\mathbf{1c}]_0} + \frac{1}{K\epsilon[\mathbf{1c}]_0[A]_0} \quad (13)$$

Here $[A]_0$ and $[\mathbf{1c}]_0$ are the initial concentrations of the acceptor and donor respectively, d is the absorbance of the donor-acceptor mixture at λ_{CT} ; The molar extinction coefficient, ϵ , is not quite that of the complex. The Benesi-Hildebrand [22] method is an approximation that we have used many times and it gives decent answers. But the extinction coefficient is really a different one between the complex and free species that absorbs at the same wavelength. K is the formation constant of the complex. Eq. (13) is valid [22] under the condition $[\mathbf{1c}]_0 \gg [A]_0$ for 1:1 donor-acceptor complexes. The intensity in the visible portion of the absorption band, measured against the solvent as reference, increases systematically with gradual addition of **1c** dye. Thus, it is definitely established in this work that the systematic increase in intensity of the broad 400–700 nm absorption band is due to 1:1 molecular complex formation between these acceptors of electrons and **1c**. This indicates complex formation. The equilibrium constant values calculated using the BH model, is only an approximation. Absorbance data for [60]fullerene/**1c** and [70]fullerene/**1c** systems in toluene medium are given in Table 2. In all the cases very good linear plots according to Eq. (13) are obtained, one typical case is being shown in Fig. 6. The correlation coefficients of all such plots were above 0.90. Formation constants for the complexes of **1c** with all the five acceptors including [60]- and [70]fullerenes (determined from the BH plots) in toluene are summarized in Table 2. It is observed that **1c** binds most tightly with *o*-chloranil instead of fullerenes. But in earlier case with **1a** [12] we find the reverse is true. This is probably because of the insertion of phenolic OH group at the *para* position of *meso*-phenyl substitution [11]. As phenol OH group increases the interacting ability of such small molecules due to formation of H-bond along with the normal π - π interaction. Again here we find **1c** binds [70]fullerene slightly more strongly rather than [60]fullerene while the reverse is observed in case of **1a** [12]. However **1b** [11] shows abnormally

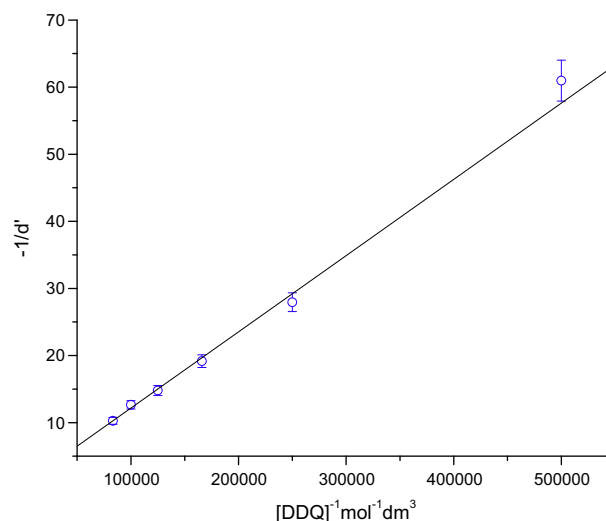


Fig. 6. Benesi-Hildebrand plot for the complex of DDQ with **1c** at 293 K.

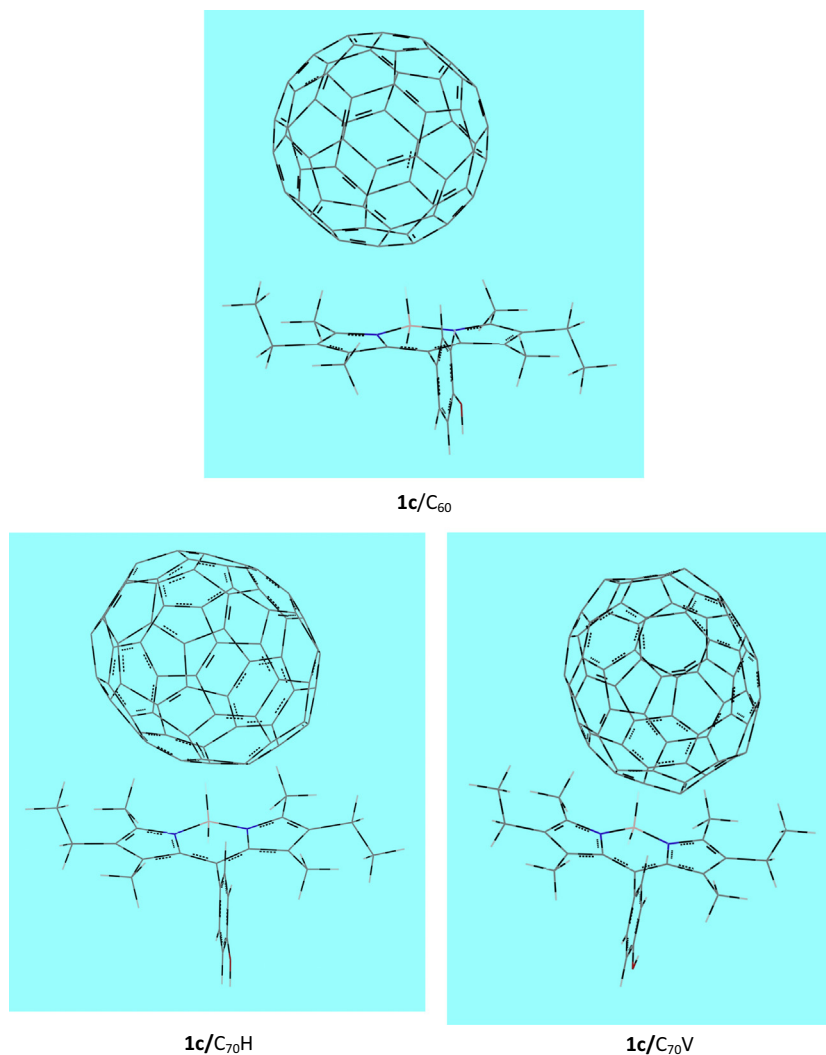


Fig. 7. Monte Carlo global minimum conformer of (a) C₆₀/1c and (b) horizontal and (c) vertical global minimum conformers of C₇₀/1c systems in gas phase.

high binding ability with [70]fullerene in toluene. DFT optimized structures of [60]fullerene/1c and [70]fullerene/1c complexes are shown in Fig. 7. In interpreting this observation it has been assumed that during formation of donor–acceptor complex, the acceptor would interact strongly with donor only when the donor molecule arranges itself parallel to the π -belt region of the acceptor molecule. In case of [70]fullerene/1c complex, it is observed that the acceptor molecule is in a somewhat favourable parallel orientation with respect to the donor ring only when [70]fullerene ring is horizontally placed (in Fig. 7b). In horizontal orientation 6:6 ring juncture of [70]fullerene lying parallel to the 1c BODIPY chromophore. But when the [70]fullerene ring is placed vertically (in Fig. 7c) then it is observed that the 6:5 ring juncture of [70]fullerene lying parallel to 1c, thus effective interaction can not takes place to such an extent. This probably minimises the binding ability of [70]fullerene with 1c compare to that of 1b. As illustrated in Fig. 7(a), the [60]fullerene molecule is precisely centered over the 1c moiety with donor–acceptor separation distance of only 3.609 Å. As expected for a donor–acceptor interaction, there are no significant changes in the bond distances and angles of the complexes relative to those found in unassociated fullerene and 1c structures. However, [70]fullerene unit is not lying parallel to the dye molecule though the donor–acceptor separation distance in case of [70]fullerene/1c complex is ~3.607 Å. With its band of hexagonal rings, the equatorial region

of [70]fullerene molecule is flatter than [60]fullerene-like polar regions. So in order to maximizing donor–acceptor interaction, [70]fullerene molecule become slightly out of plane of the 1c moiety leading to weak complexation in comparison to 1b.

Conclusions

- (i) Ground state charge transfer complex formation between 1c and chloranils and fullerenes are established.
- (ii) The $(h\nu_{CT} - E_A'')$ dependencies of the 1c complexes with the above series of acceptors have been obtained and from their variation the vertical ionization potential of 1c has been obtained in toluene medium.
- (iii) With decreasing values of the electron affinities, the CT band shifts to the lower energy side and the degree of the CT transition decreases.
- (iv) Among all the complexes investigated in present study, the *o*-chloranil/1c complex exhibit the highest ground state resonance energy.
- (v) 1c has slightly higher ionization potential compared to that of 1a, still, 1c compound is much better electron donor than those of 1a and 1b as reflected from resonance energy and degree of charge transfer values.

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