



## Effect of substitution of methanoboron difluoride derivatives on non-covalent interactions with tetraphenylporphyrin

C. Pal

Department of Chemistry, Ramananda College, Bishnupur, Bankura, 722122

### Abstract

Tetraphenylporphyrin (TPP) forms non-covalent supra-molecular complexes with methanoboron difluoride (MBDF) derivatives in dichloromethane. The photo-chemical properties of the association equilibrium of free TPP and MBDFs with the respective supra-molecular complexes were investigated in the ground state. There is formation of isosbestic points which had been taken as proof of the existence of equilibrium between the absorbing species. Monte Carlo simulation and Density functional theory calculation established the experimental results of non-covalent interactions in terms of loss of planarity and frontier molecular orbital calculations defines the electron donor and acceptor. The direction of electron flow is confirmed by the electrochemical indices. The electron rich substituent in MBDF favours the non-covalent binding ability between TPP and MBDF. Both H-bonding and charge transfer interactions are primarily responsible in stabilising these complexes.

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### Introduction

Porphyrins and their derivatives have been extensively studied for numerous applications due to their exceptional electrochemical and photo-physical properties. The macrocycle of porphyrin is one of the most extravagantly explored because of their importance in photochemistry, photosensitization (Kalyanasundaram *et al.*, 1987), biochemistry, biomedical (Chen *et al.*, 2021) and catalysis (Ni *et al.*, 1987). Synthetic porphyrins also have received substantial attention due to their usefulness in light harvesting materials for the construction of photovoltaic cells (Yeo *et al.*, 2017; Loewe *et al.*, 2002). Though, non-covalent interactions are quite weak but multiple intermolecular interactions cooperate in binding to form stable complexes (Mulder *et al.*, 2004; Badjić *et al.*, 2005; Pal *et al.*, 2016). Supramolecular architectures of porphyrins and their derivatives can be prepared by self-assembly based on non-covalent interaction and molecular

recognition (Wu *et al.*, 2021; Villari *et al.*, 2012; Drain *et al.*, 2009; Chaudhuri *et al.*, 2010).

The supramolecular interactions between porphyrin and neutral  $\pi$ -acceptors have been studied for years. In recent times the chemistry of porphyrin-metal complexes is of great interest (Brothers, 2000; Brothers, 2001; Kadish, 2011). The interaction of free base porphyrins with halogen substituted borane has been the topic of attention (Belcher *et al.*, 1994; Mohajer *et al.*, 2004; Brothers, 2008; Pal *et al.*, 2017). It has been revealed that the reaction of free base *meso*-tetraphenylporphyrin (TPP) with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (boron trifluoride diethyl etherate) in wet chlorobenzene yielded a boronated adduct and in this compound two adjacent pyrrole nitrogens are bonded to each B atom with loss of -NH proton (Belcher *et al.*, 1994).

The H-bond formation between fluorine of  $\text{BF}_3$  and -NH protons of porphyrin was also confirmed by Mohajer *et al.*, 2004 in the adduct of  $\text{BF}_3$  and free base porphyrin. In the complex of methanoboron difluoride (MBDF) and Cu-phthalocyanine non-covalent electrostatic interaction was confirmed by our group (Pal *et al.*, 2017).

In this communication the effect of substituents at methanoboron difluoride moiety on the non-covalent supramolecular interaction between tetraphenylporphyrin and MBDF derivatives (Fig. 1) in ground state have been photo-physically investigated. Spectroscopic investigation of the adducts has been executed and well supported by Monte Carlo simulation and density functional theory (DFT) based computation via reactivity indices and frontier molecular orbital (FMO) descriptors. Our group had previously studied the effect of substituents at porphyrin moiety in TPP and MBDF supramolecular interaction (Pal *et al.*, 2016). The study of the effect of substitution at MBDF moiety enriches the exploration of supramolecular interaction between TPP and MBDF. The trend in equilibrium constant by varying substituent in both the moieties firmly establishes the interaction type viz., charge transfer and H-bonding as well. The need for global minima search among several local minima is accomplished here by Monte Carlo simulation which lacks in our former study. As compared to our previous study the use electrochemical indices plays vital role in establishing the direction of charge flow in this work and may be used as a tool for studying these types of interactions.

## Materials and methods

Dichloromethane was used as solvent of spectroscopic grade from Merck, India. According to the reported techniques the three methanoboron difluorides (Zhang *et al.*, 2006) and tetraphenylporphyrin (Adler *et al.* 1967) used were synthesized. In all the spectral measurements the concentration of MBDFs and TPP were taken in the range  $10^{-5}$  and  $10^{-6}$  M respectively.

Shimadzu UV 1800 series PC spectrophotometer fitted with an electronic temperature controller unit (TCC/240 A) was used for absorption (UV/Vis) spectral measurements. The steady state fluorescence spectra were reported with a temperature controlled Hitachi F-7000 spectrofluorometer. Constant temperature bath (Heto

Holten, Denmark) was used to control the temperature within  $\pm 0.1$  K.

Using Spartan'14 molecular modelling software of Wavefunction, Inc., USA the computer simulations were executed. Merck molecular force-field calculations were implemented by using the Monte Carlo simulation to search global minima for all the optimized adducts. Gaussian 09 (Linux), Gaussian, Inc. (USA), software was used for the DFT calculations. MPW1PW91/6-31G functional was used to calculate the single point geometries and FMOs for all the free systems and their adducts.

## Results and discussion

### Ground state interactions

All the MBDF derivatives exhibit a strong one photon absorption ( $\epsilon > 20,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the 350 nm - 450 nm range in dichloromethane. This corresponding band is due to  $\pi \rightarrow \pi^*$  transition and the band is somewhat narrow (50 nm - 75 nm at half-width). Only monomeric species of MBDFs are present in this working concentration range around 15  $\mu\text{M}$ . This is due to the fact that the absorption changes linearly with change in concentration without any variation in spectrum. Interaction of substituted MBDF systems to the electron rich porphyrin (TPP) was examined by visible absorption spectroscopy. Three solutions of the MBDFs (MBDF2, MBDF4 and MBDF5) were titrated separately with a stock solution of TPP in dichloromethane medium. Fig. 2 shows appearance of an isosbestic point for all the MBDF systems and intensity of maximum absorption of MBDFs reduced by addition of the solution of TPP. Table I described the isosbestic points in diverse regions of the spectra on interaction of TPP with MBDF2, MBDF4 and MBDF5 in dichloromethane. Formation of isosbestic point is proof of the existence of equilibrium between two absorbing species (Hemdan *et al.*, 2019). Thus, in the ground state all the MBDFs interacts with TPP and form stable equilibrium with the respective adduct in dichloromethane. In Fig. 2, on the shorter wave length side of all the isosbestic points the peaks are corresponding to the strong  $S_0$  to  $S_1$  absorption of MBDFs and on addition of TPP in the solution of MBDF the intensity of maximum absorption diminishes drastically. And on the other side of the isosbestic point the peaks arises due to the formation of adduct of MBDF and TPP. The electron density could swing from the electron rich TPP to the electron deficient MBDFs and the

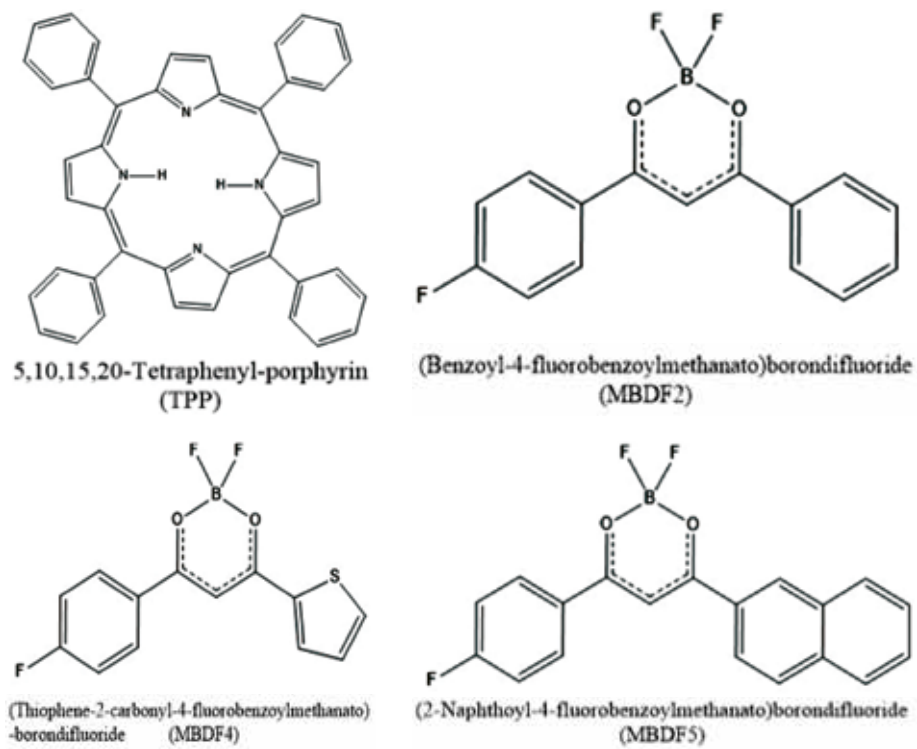


Fig. 1. Structures of the compounds used

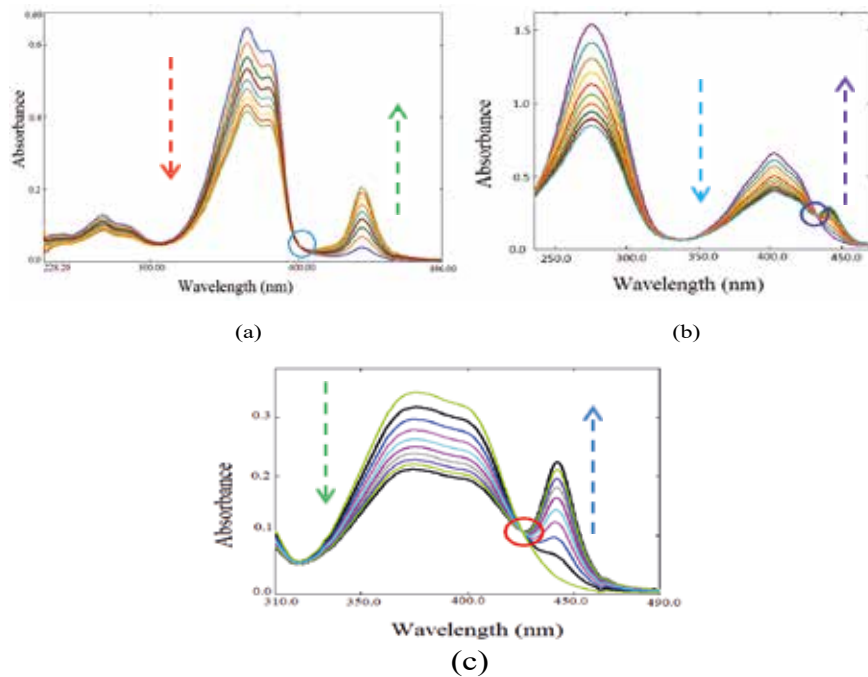


Fig. 2. Absorption spectra due to interaction of (a) MBDF2 (15.9  $\mu\text{M}$ ) (b) MBDF4 (15.6  $\mu\text{M}$ ) (c) MBDF5 (15.2  $\mu\text{M}$ ) with TPP (concentration was varied from 0.0  $\mu\text{M}$  to 1.23  $\mu\text{M}$ ) in dichloromethane medium. Isosbestic points are shown within the circle

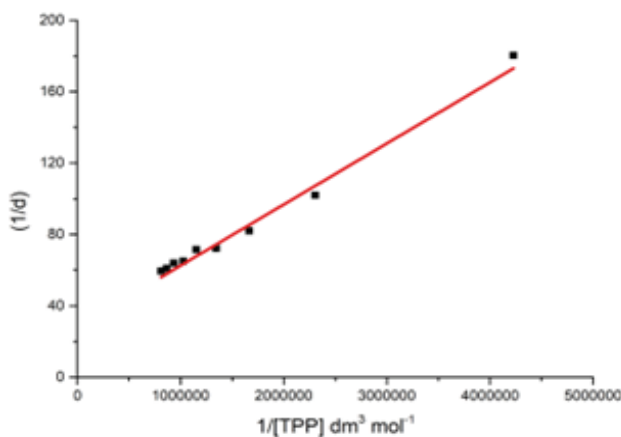
F-atoms of MBDFs can take part in H-bonding with pyrrolic N-H protons of the porphyrin. Thus, this may be of electron donor-acceptor,  $\pi$ -stacking and H-bonding type interaction. These interactions are well explored and supported by theoretical calculations in theoretical analysis section.

#### Determination of equilibrium constants

Benesi–Hildebrand equation (Benesi *et al.*, 1949) of the form (eq. 1) was used to determine the equilibrium constant reported in Table I corresponding to TPP/MBDF interaction in ground state

$$\frac{1}{d} = \frac{1}{\epsilon[\text{MBDF}]_0} + \frac{1}{K \{ \epsilon[\text{MBDF}]_0 \} [\text{TPP}]} \quad (1)$$

where [TPP] is the concentration of the TPP and  $[\text{MBDF}]_0$  is of the MBDF solution respectively,  $d$  is the absorbance of the newly formed complex and  $d = [d_{\text{mix}} - d_{\text{MBDF}}^0 - d_{\text{TPP}}^0]$ , where  $d_{\text{mix}}$ ,  $d_{\text{MBDF}}^0$  and  $d_{\text{TPP}}^0$  are the absorbance of the TPP/MBDF mixture, the respective methanato boron difluoride solution and the TPP solution at the same molar concentration present in the mixture at the same wavelength against solvent as reference. The molar absorptivity  $\epsilon$  is that of the complex and  $K$  is the equilibrium constant of the complex. The Benesi–Hildebrand (Benesi *et al.*, 1949) method is an adequate approximation



**Fig. 3.** BH plot of TPP/MBDF2 interacting system in methylene chloride

and it gives sensible values for equilibrium constant ( $K$ ), has been exploited many measurements. 1:1 molecular complex formation between the TPP/MBDF was recognized by the linear BH plot at Fig. 3. Pearson's correlation coefficient and coefficient of determination (R-square) are 0.99461 and 0.98772 respectively, indicates a good quality fit. Linear regression was used to get the intercept and the slope.

The complex formation between TPP and MBDF4 is the most proficient as compared to the other interacting systems in the ground state and the equilibrium constant has the order  $K_{\text{TPP/MBDF4}} > K_{\text{TPP/MBDF2}} > K_{\text{TPP/MBDF5}}$ . The non-covalent H-bonding interaction between the F atom of MBDF and N-H atom of TPP is the strongest in case of TPP/MBDF4 system. The electron density at MBDF ring increases drastically due to the +R effect of the thiophenyl group in MBDF4 which facilitates strongest interaction among the others. On the other hand, the naphthyl substituted MBDF5 has the lowest binding constant due to predominant steric effect of the naphthyl group.

#### Theoretical analysis

Monte Carlo conformational search protocol (Chang *et al.*, 1989; Kong *et al.*, 2000) was used for these complexes. Density based geometry optimization calculations of the adduct structures are mostly used for studying weak intermolecular interactions such as CT, van der Waals, H-bonding, and hydrophobic interactions (Cantrill *et al.*, 2000; Bhasikuttan *et al.*, 2007). It is well known that all the optimization methods employing quantum and semi classical calculations find the local minima or transition structures near to the starting structure. However, DFT based calculations have disadvantages related to the best choice of functional for the system of interest. Many DFT methods provide poor result for weakly-bound intermolecular complexes and hydrogen bonded systems (Sholl and Steckel 2011). The conformational analysis is done for the global minimum among several local minima and energy barriers. Monte Carlo protocol (Chang *et al.*, 1989) is a well-established tool for conformational global minima searching of weakly-bonded adducts and were implemented here based on force-field molecular mechanics (Kong *et al.*, 2000), accessible in the Spartan 14 package. Conformational analysis and structural optimization of these complexes were accomplished by molecular mechanics Monte Carlo simulation and the single point energy calculations were performed by using MPW1PW91/6-31G level of DFT. Fig. 4 presents optimised geometries of the three complexes.

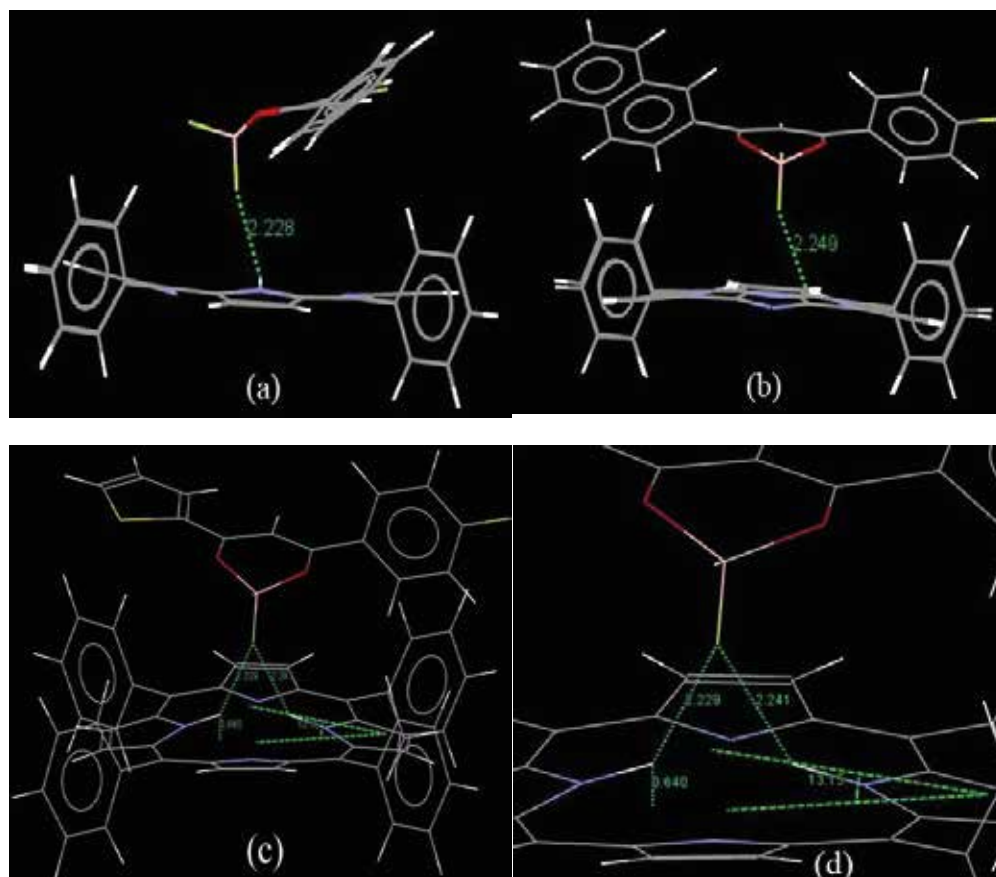


Fig. 4. Orientation of the adduct of (a) TPP/MBDF2 (b) TPP/MBDF5 (c) TPP/MBDF4 (d) TPP/MBDF4 (Zoom in view) interacting systems in optimized ground state geometry showing the interatomic distances in Å

Table I. Isosbestic point appeared on interaction of TPP with MBDFs and the ground state equilibrium constants for the corresponding three complexes

System	Absorption isosbestic point at wavelength (nm)	Ground state equilibrium constant (K) $\times 10^{-5}$
TPP/MBDF2	400.3	8.21
TPP/MBDF4	432.4	27.1
TPP/MBDF5	425.6	3.2

**Table II. Parameters of the optimized ground state geometry of the adducts**

System	Angles		H bond distance (Å)		distance (Å) of H atom of N-H <sup>1</sup> moiety with the plane of porphyrin ring
	N-H moiety with plane of porphyrin ring	B-F moiety with methanato ring	N-H <sup>1</sup>	N-H <sup>2</sup>	
TPP/MBDF2	12.51°	33.23 °	2.228	2.237	0.561
TPP/MBDF4	13.15 °	34.19 °	2.229	2.241	0.640
TPP/MBDF5	11.60 °	32.89 °	2.249	2.258	0.554

**Table III. HOMO-LUMO energy parameters (electrochemical indices) of the molecules**

Moiety	Electronic chemical Potential ( $\mu$ ) (eV)	Global electrophilicity index ( $\omega$ ) (eV)	Global nucleophilicity index (N) (eV)
TPP	-3.56	2.31	4.55
MBDF2	-5.10	3.34	2.44
MBDF4	-5.10	3.54	2.54
MBDF5	-4.83	3.45	2.97

There is a possibility of hydrogen bonding between the N-H protons of porphyrin moiety and B-F fluorine of MBDFs which is in close proximity to each other. In the free State the N-H protons are in a same plane with the porphyrin core. But in the complex the N-H protons go out of plane towards the F-atom of MBDFs which is adjacent to the porphyrin core and is within H-bonding distance. Whereas the  $-\text{O}-(\text{BF}_2)-\text{O}-$  group also goes out of plane towards the pyrrolic proton (Fig. 4a) which was in plane with the methanato group before adduct formation. Table II illustrates the amount of deviation from the planes of the said groups and the deviation is highest in case of MBDF4 due to better H-bonding interaction. All the different substituents of MBDF increase electron density at MBDF ring but the +R effect of thiophenyl group in MBDF4 is most effective than the +I effect of phenyl and

naphthyl group. Due to the greater electron density the F-atom of  $-\text{O}-(\text{BF}_2)-\text{O}-$  group becomes more negatively charged thus facilitates better electrostatic interaction with the N-H protons of TPP. The H-bonding interaction is not in agreement with the experimental trend of equilibrium constants. The reason for that is not only the hydrogen bonding but the donor to acceptor charge transfer is primarily responsible for stability of these complexes. Thiophenyl group is more electron rich as compared to the phenyl group that facilitates better charge transfer in TPP/MBDF4 complex. The charge transfer is least in case of MBDF5 due to the steric effect of naphthyl group. When the donor molecule arranges itself parallel to the  $\pi$ -belt region of the acceptor molecule only then acceptor should interact strongly with the donor molecule. The molecular orbitals of donor and accep-

tor molecules can overlap effectively when they are able to approach quite close to each other without much steric hindrance. Both electron donor acceptor (EDA) charge transfer interaction and the hydrogen bonding contribute amply in the stability of these complexes. TPP/MBDF4 complex is favoured by both these interactions and evidently has the highest observed equilibrium constant.

Electronic chemical potential ( $\mu$ ), electrophilicity index ( $\omega$ ) and nucleophilicity index (N) of the individual isolated molecules has been calculated and displayed in Table III. The electronic chemical potential ( $\mu$ ) is the index to determine the direction of the electronic flux during the charge transfer within the system in its ground state (Pérez *et al.*, 2003). Higher electronic chemical potential ( $\mu$ ) of TPP than MBDF derivatives indicates that charge transfer occurs from TPP to

MBDFs. The global electrophilicity index ( $\omega$ ) (Pérez *et al.*, 2003; Chattaraj *et al.*, 2006) measures the stabilization in energy when the system acquires an additional electronic charge ( $\Delta N$ ) from the environment. Those molecules are considered as strong electrophiles for which  $\omega > 1.5$  eV. Electrophilicity indexes ( $\omega$ ) of MBDF derivatives are way better than 1.5 eV. Thus, they serve as good acceptor during charge transfer interaction with TPP. The global nucleophilicity (N) index (Domingo *et al.*, 2008) value of TPP is 4.55 eV.  $N > 3.0$  eV are said to be strong nucleophiles and thus TPP acts as a donor during charge transfer.

#### Frontier molecular orbital interactions

The supramolecular interaction is appropriately understood by analyzing the interaction between the frontier molecular

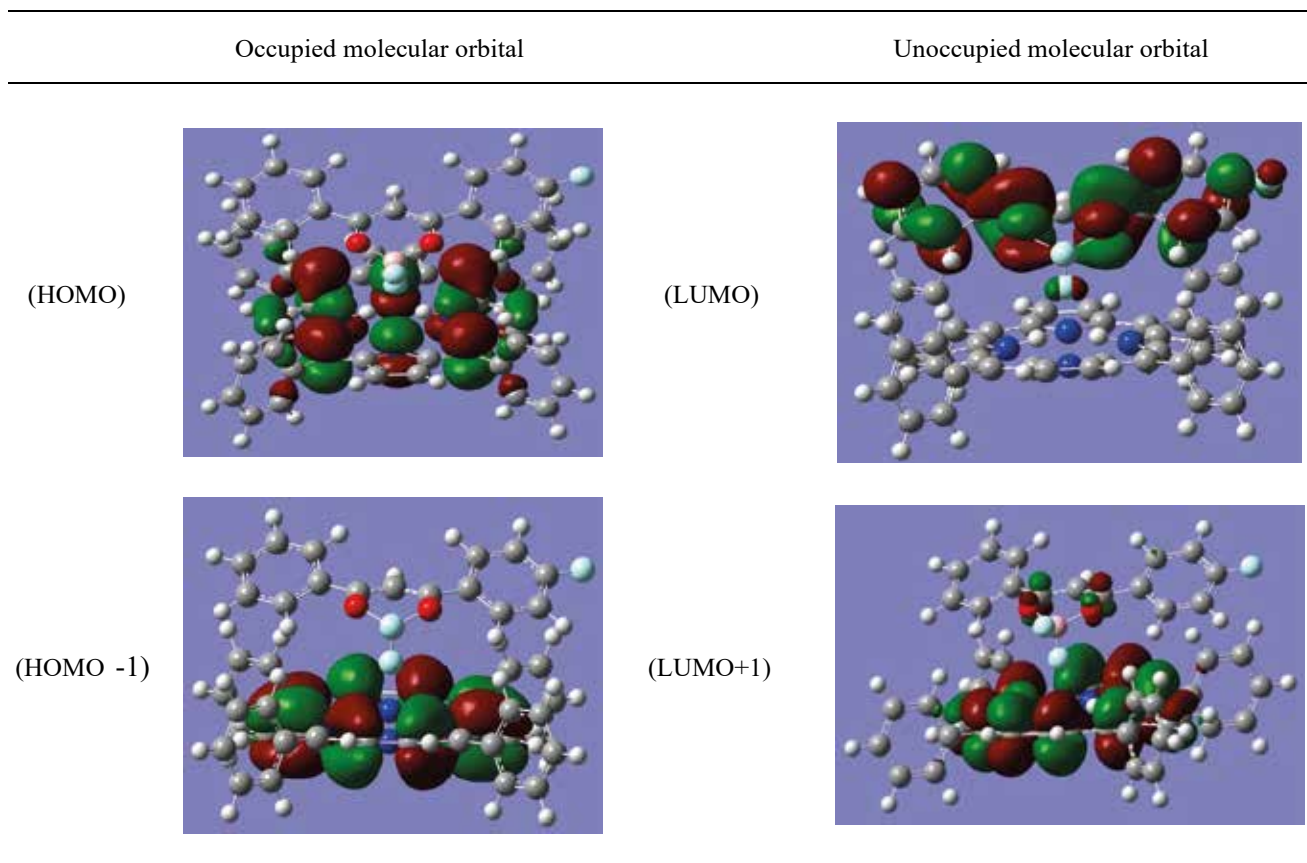


Fig. 5. Frontier molecular orbital pictures of TPP/MBDF2 interacting system

orbitals (HOMO and LUMO) of the two interacting moieties in the adducts such as the donor and the acceptor. MPW1PW91/6-31G level of density functional theory was employed to study the HOMO-LUMO interactions. Fig. 5 illustrates that the HOMO of the complexes resides primarily on TPP while LUMO is located on the acceptor MBDF2 moiety, mostly. This has reasonably substantiated the direction of electron flow in the EDA (electron donor acceptor) complex with the electron rich TPP and electron deficient MBDFs. Hence, the frontier molecular orbital picture illustrates a pictorial description of charge transfer interaction which occurs between haloborane MBDF and free base TPP.

### Conclusion

Substitutions in MBDF moiety affect the binding ability with TPP significantly. All the three MBDFs form stable absorption isobestic on titrating with TPP. DFT based geometry optimization and conformational analysis, frontier molecular orbital calculation and electrochemical indices well justifies the experimental finding of formation of ground state equilibrium. Hydrogen bonding, charge transfer and steric congestion effectively determine the binding ability as evident from the fact that the electron rich substituent in MBDF with less steric congestion favours the binding between TPP and MBDF and has the highest equilibrium constant.

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### Declaration of Competing Interest

The author declared no conflict of interests.

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