

Original research article

Adsorption studies of dye molecule on two-dimensional assembly of porphyrin using density functional theory

Rahul Suresh^{1,*}, R. Rajaramakrishna², S. Vijayakumar^{3,*}

¹ International Research Center of Spectroscopy and Quantum Chemistry—IRC SQC, Siberian Federal University, 79 Svobodny pr., 660041 Krasnoyarsk, Russia

² Siberian Federal University, 79 Svobodny pr., 660041 Krasnoyarsk, Russia

³ Department of Medical Physics, Bharathiar University, Coimbatore 641046, India

* Corresponding authors: Rahul Suresh, drrahulsuresh@gmail.com; S. Vijayakumar, svijayakumar@buc.edu.in

Abstract: Highly toxic dye molecules can be found in trace amounts in the treated effluent from several industrial wastes. A challenging research area of this decade is the dye treatment and adsorption from the effluents of these industries using low-cost alternative adsorbents. Recent studies have demonstrated the effectiveness of metal oxides and porous materials in the adsorption of dye, so we have taken into consideration an organic porous material made with metal free porphyrin. The adsorption of dye molecules on the surface of the porphyrin sheet is investigated. Porphyrin is an organic substance with several special properties. Density functional theory (DFT) is used to investigate the adsorption of charged and neutral dye, as well as complex heavy metal dye, on the surface of porphyrin sheets. Positive dye has a higher affinity for the adsorbent than negative dye, according to the data on adsorption; however, complex dye has a higher adsorption energy than the other dyes, which is consistent with the cohesive energy of the PS-dye complex. In the present work the adsorbing capacity of PS for different dye molecules is demonstrated by the topological analysis and DFT calculations on the electronic structure.

Keywords: adsorption; dye; porphyrin; covalent organic frameworks; DFT

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1. Introduction

Dye molecules plays a vital role in textiles and dyeing industries as much as one thousand tons of biodegradable dyes are released into environment annually and hence become the one of the largest group of organic pollutants in the atmosphere^[1]. It is necessary to remove the toxic materials even before it reach the environment to save the future of our ecosystem. There are several methods reported to degrade dye molecules like photocatalysis, ozonation, adsorption, etc.^[2]. In this work, we have reported the adsorption method to remove the dye molecules using covalent organic frameworks. The porphyrin molecule is arranged in a two-dimensional manner covalently linked to each other. We have already reported the significance of porphyrin and its derivatives which depict the adsorption ability of porphyrin derivatives such as heme and porphyrin sheets for toxic gas molecules^[3], greenhouse gases and alkali metals^[4].

2. Materials and methods

The porphyrin subunits are connected to one another through covalent bonds appearing to be a planar

two-dimensional array. Here, we have considered 3×3 porphyrin sheets (**Figure 1**).

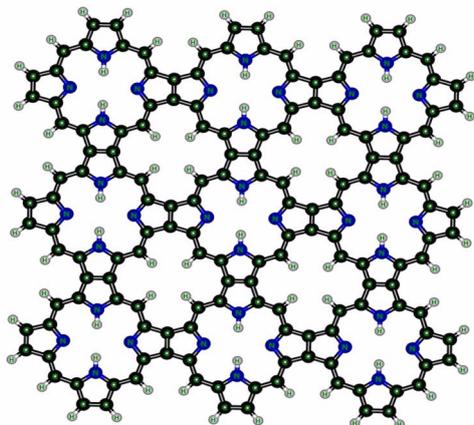


Figure 1. Porphyrin subunits covalently bonded to each other forming porphyrin sheet (PS) optimized at wb97xd/6-31g** level of theory in water medium.

The structure was optimized in water medium using Gaussian09^[5] at wb97xd/6-31g** level of theory which includes Grimme's dispersion and also the long range interactions. The relaxed structure of PS is interacted with negatively charged dye molecule methyl orange (MO), positively charged dye molecule methyl blue (MB) and neutral charged dye molecule p-aminoazobenzene (PAAB) (**Figure 2**).

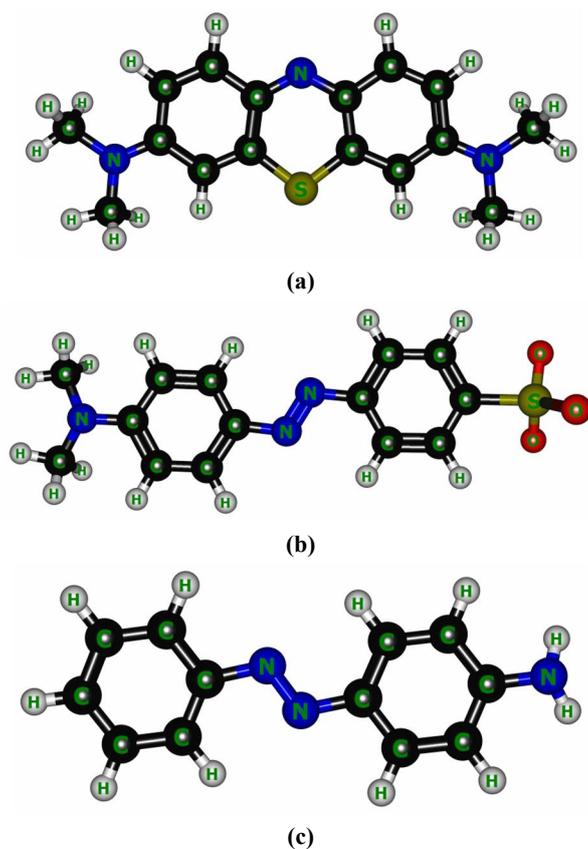


Figure 2. Structure of dye molecules interacted with the PS. (a) methylene blue (MB); (b) methyl orange (MO); (c) p-aminoazobenzene (PAAB).

Apart from the charged and neutral dye, we have only studied the adsorption energy of the PS for Ruthenium dye (RuD) which is largely used as excellent photosensitizers in the application of DSSCs (**Figure**

3). The absence of imaginary frequency confirms the stability of the structure at the energy minima of the potential surface^[6].

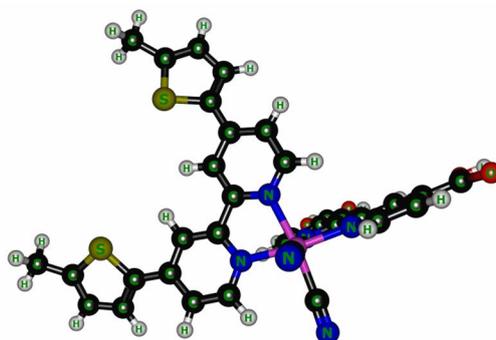


Figure 3. Structure of Ruthenium dye (RuD) optimized at wb97xd/6-31g** level of theory.

The charge transfer properties and bonding orbitals details between the dye molecule and the PS were calculated using natural bonding orbital (NBO) analysis. The Quantum Theory of Atoms in Molecules (QTAIM) analysis was performed to determine the nature and strength of the bonding between dye molecule and PS and the bonding parameters are determined from the electron density difference plot (EDD) using Multiwfn program^[7].

3. Discussion

The structure of PS is shown in **Figure 1** and it reveals the planar nature of porphyrin. The length of the sheet is found to be 27.23 Å with a cavity region at the juncture of four porphyrin subunits. The interatomic distance between H-atoms in the porphyrin region is 2.21 Å whereas the distance between H-atoms in the cavity region varies between 3.00 and 3.10 Å. The dye molecules are interacted with different orientation of the molecule and the minimized structures are reported in this manuscript (**Figure 4**).

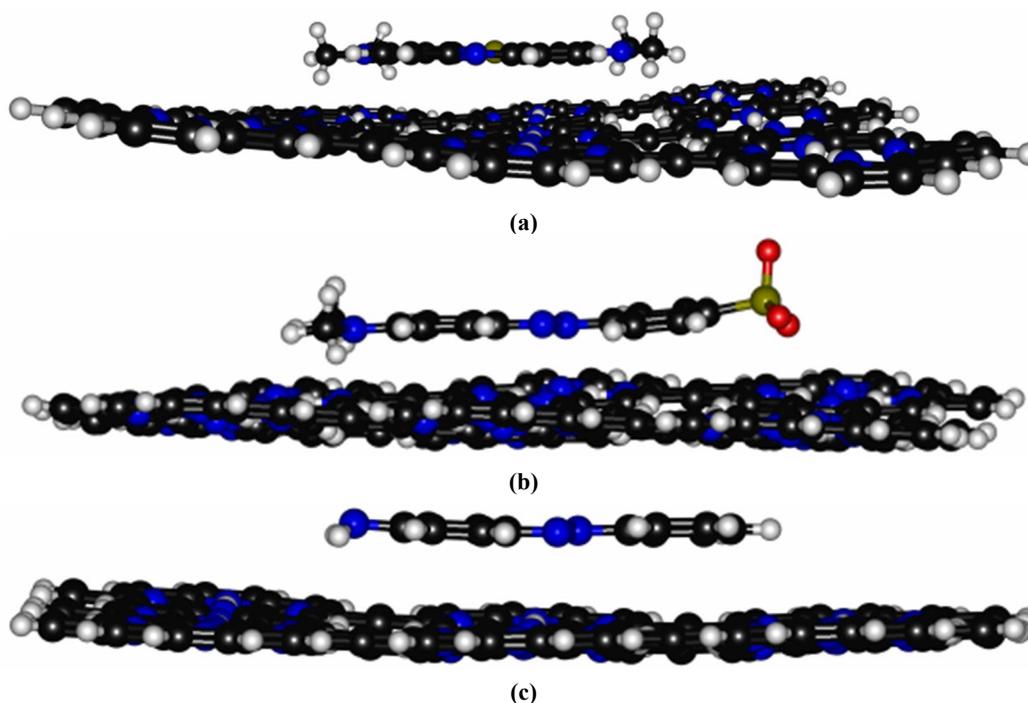


Figure 4. Relaxed structure of dye-PS complexes optimized at wb97xd/6-31g** level of theory in water medium (a) MB-PS; (b) MO-PS; (c) PAAB-PS.

From **Figure 4**, it is very evident that the planar structure of PS is not completely distorted on interaction with dye molecules. It is important to know that the dye molecules ruffle only the planar structure of the PS but not the atoms and the stability of the PS substrate. The dye molecule interacted with the PS at different orientations assemble themselves parallel to the sheet making more room for interaction between the PS and the dye molecule. The RuD molecule on interaction with the PS (**Figure 5**), the dye molecule completely distorts the planar structure of PS. The cohesive energy is computed for all the complexes using the formula

$$E_c = \frac{(E_{Total} - E_{PS} - nE_{AM})}{n}$$

and tabulated in **Table 1**. The cohesive energy is the amount of energy required to break the complex into isolated molecules.

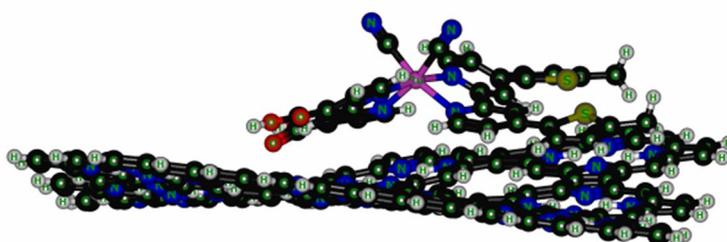


Figure 5. Relaxed structure of RuD-PS complex optimized at wb97xd/6-31g** level of theory.

From **Table 1**, the cohesive energy is maximum for MB followed by MO and PAAB, which indicates that complex formed between the PS and the positive dye is much stronger than the other complexes.

Table 1. Cohesive energy calculated for PS-dye complex optimized at wb97xd/6-31g** level of theory.

Structure	Cohesive energy EC (eV)
PS-MB	-1.63
PS-MO	-1.36
PS-PAAB	-1.08

The interaction energy including basis set superposition error (BSSE) corrections between the PS and dye molecules are calculated using counterpoise method suggested by Boys and Bernardi^[8]. The adsorption energy was calculated using the formula

$$E_{ads} = E_{PSDYE} - (E_{PS}^{PSDYE} + E_{DYE}^{PSAM})$$

where E_{ads} is the total adsorption energy of dye molecules on PS, E_{PSDYE} is the total energy of the complex including dye molecule and PS, E_{PS}^{PSDYE} is the energy of PS and E_{DYE}^{PSAM} is the energy of the dye molecules. The counterpoise method used to calculate the adsorption energy excluding the solvent medium gives the magnitude of the adsorption energy with the nearest real value. The adsorption energy of dye molecules interacted with PS is tabulates in **Table 2**.

Table 2. Adsorption energy calculated for PS-dye complex optimized at wb97xd/6-31g** level of theory in the absence of solvent.

Structure	Adsorption energy (eV)
PS-MB	-2.17
PS-MO	-1.63
PS-PAAB	-1.08
PS-RuD	-2.72

The adsorption energy is maximum for RuD dye (-2.72 eV) with an average adsorption height of 2.60 Å. At the same time, the positive dye MB is having more affinity towards PS with an adsorption energy of -2.17 eV at an adsorption height 2.42 Å. The negative dye MO shows decrease in adsorption energy (-1.63 eV) with respect to MB with no major change in the adsorption height (2.40 Å) whereas the adsorption energy of MO is higher compared to that of neutral dye PAAB. The PAAB records the least adsorption energy of -1.08 eV with highest adsorption height of 2.87 Å. Molla et al. performed the adsorption studies of MB and MO on graphene oxide (GO) using Ab initio molecular dynamics (AIMD) simulations^[9].

From their work, the adsorption energy between MB/MO and GO is found to be -2.25 and -1.45 eV/molecule which is approximately near our findings. Similarly, Minitha et al. demonstrated the adsorption of MB and MO on reduced graphene oxide (rGO) and found the adsorption energy to be -2.60 and -0.35 eV respectively^[10].

It says that graphene appears to be a strong adsorbent for positive dye, based on the results given for MB/GO (-2.25 eV), and MB/rGO (-2.60 eV). Following and PS appear to be strong candidates for negative dye, based on the RuD/PS (-2.71 eV) and MO/PS (-1.63 eV). As for the PS, the results indicate that the material can perform adsorption of positive and negative dyes, according to the adsorption energy. However, the magnitude of our findings in absence of continuum model are only the approximation of the actual results.

The electronic properties such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are calculated using natural bonding orbital (NBO) analysis. The energy gap was calculated from

$$E_{HOMO-LUMO} = E_{HOMO} - E_{LUMO}$$

where E_{HOMO} and E_{LUMO} are HOMO and LUMO energy levels, respectively. **Table 3** reports the HOMO-LUMO level and energy gap of PS and dye adsorbed PS complexes.

Table 3. Electronic properties of the material calculated using natural bonding orbital (NBO) analysis. Chemical reactivity parameters χ -electronegativity, η -hardness, μ -chemical potential and ω -electrophilicity index in eV for heme-gas complexes.

Structure	HOMO (eV)	LUMO	Energy gap	Fermi energy	χ	η	μ	ω
PS	-6.02	-2.24	-3.78	-4.13	7.14	4.9	-4.13	41.78
PS-MO	-5.96	-2.18	-3.78	-4.07	7.05	4.87	-4.07	40.33
PS-MB	-6.05	-2.28	-3.77	-4.16	7.19	4.91	-4.16	42.58
PS-PAAB	-5.99	-2.2	-3.79	-4.0	7.09	4.89	-4.09	41.00
PS-RuD	-6.03	-2.26	-3.77	-4.14	7.16	4.9	-4.14	42.09

Chemical reactivity parameters χ -electronegativity, η -hardness, μ -chemical potential and ω -electrophilicity index in eV for heme-gas complexes are also tabulated^[11]. The chemical potential is the ability of a system to exchange electrons with the surrounding and is calculated using.

$$\mu = -\frac{(E_{HOMO} + E_{LUMO})}{2}$$

The stability of the system with the external resistance is denoted as hardness calculated using Koopman's theorem^[12].

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

The reactivity of the material is the electrophilicity of the material calculated using

$$\omega = \frac{\mu^2}{2\eta}$$

From **Table 3**, the HOMO and LUMO of PS is found to be -6.02 and -2.24 eV which further varies on interaction with dye molecules. The HOMO and LUMO level increases on interaction with MB dye (-6.05 and -2.28 eV) whereas the decreases to -5.96 and -2.18 eV on interaction with negative dye MO. For interaction with neutral dye, the HOMO-LUMO level is less than PS but lies between that of MB and MO. The adsorption energy for RuD is approximately near that of positive dye. The HOMO-LUMO energy gap is almost close to PS for all the complexes which indicate that the adsorption of dye does not affect the energy gaps of the PS molecule. The fermi energy is the state of occupying an electronic state calculated using the formula.

$$Fermi\ Energy = E_{HOMO} + \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

From **Table 3**, the fermi energy is maximum for MB interacted PS and least for PAAB interacted PS. The global indices calculated show no major changes in the value proving that the PS material is stable and do not undergo any chemical changes on adsorption of dye molecules and make PS a suitable material for adsorption properties.

The topological analysis and charge transfer between the PS and the dye molecule is determined by atomic dipole corrected Hirshfeld charges using Multiwfn^[13,14]. The topological parameters are calculated using the method proposed by Bader^[15] from the bond critical points between the PS and the dye molecules and tabulated in the **Table 4**.

Table 4. Topological analysis of dye interacted PS. Total electron density (ρ), Laplacian of electron density ($\Delta^2(\rho)$), Lagrangian Kinetic energy $G(r)$, potential energy density $V(r)$ and energy density $H(r)$.

Structure	$P(r)$	$\Delta^2(\rho)$	$G(r)$ (eV)	$V(r)$	$H(r)$
PS-MO	16.95	5.79	12.15	-9.81	23.37
PS-MB	17.42	5.69	11.06	-7.90	23.16
PS-PAAB	18.46	5.58	11.37	-8.78	25.90

The total electron density $\rho(r)$ is the molecular aspect to shift the negative charge towards a point, i.e., to transfer the electrons from an atom to another or a system to another. The trace of the second derivative of $\rho(r)$ gives the Laplacian of the electron density calculated using the Hessian matrix. The positive Laplacian density value indicates the closed shell interaction between the PS and the dye molecule, and the larger value indicates the weak electrostatic nature of the interaction. The positive $H(r)$ value indicate the non-covalent nature of the interaction and for the $H(r) > 0$ indicates the interactions to be electrostatic dominant. The electrostatic interaction energy calculated between PS and MB, MO and PAAB is found to be -16.38 , -52.99 and -10.02 kJ/mol, which is further supported by the $G(r)$ and $H(r)$ values that indicate the kinetic and potential energy density values.

4. Conclusion

The porphyrin molecules stacked in a two-dimensional array exhibit strong adsorption properties towards neutral, charged and dye molecules. The dye molecules adsorbed on the PS, cause no major changes to the HOMO-LUMO level of the substrate despite having a strong adsorption energy between the PS and dye molecules. The charge transfer between the molecules depicted the existence of weak interaction between them

adding more strength to our prediction. The above properties not only enable PS to be a good adsorbent for dye pollutants but also can be optimized for dye sensitized solar cells applications.

Author contributions

Conceptualization, RS and RR; writing—original draft preparation, RS; writing—review and editing, SV and RR. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

Abbreviations

MB	Methylene blue
PAAB	P-aminoazobenzene
MO	Methyl orange
PS	Porphyrin sheet

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