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Exploring crystal structure of 5, 10, 15, 20-tetrakis (4-iodophenyl) porphyrin; H_2 TIPP: Experimental and theoretical investigations

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ABSTRACT

The present work represents chemical preparation, characterization, and crystal structure analysis combined with computational density functional theory; DFT and hirshfeld surface analysis; HSA of 5, 10, 15, 20-tetrakis (4-iodophenyl) porphyrin; H₂TIPP. The title compound crystallizes in triclinic crystal system in space group P-1 having half molecule in asymmetric unit cell. Molecular packing seems to be controlled by various molecular interactions and has been put in evident and further addressed by HSA. The geometry obtained displays that the porphyrin core including the pyrrole rings and meso-carbon junction opts a planar geometry. However the phenyl rings containing iodine substituents are twisted from that core plane approximately perpendicular to each other and can be visualized as a slightly distorted propeller. Examining experimental and theoretical geometry confirms strong N–H•••N intramolecular hydrogen bonding involving in formation of qausi aromatic six membered rings at opposite ends inside the core, other prominent neighboring interaction exhibits interplay of N–H, H–H, C–H, C–I, and I•••I. Furthermore its quite evident those functional substituents at peripheral groups are quite flexible and directional which has improved their orientation from one dimensional to 2D and 3D supramolecular architecture. This reflects their greater role as porous solids.

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1. Introduction

This part involves predetermine the crystal engineering evaluation of self assembly models of functional tetraphenylporphyrin; (TPP). These assemblies between organic and inorganic components are sustained by various supramolecular interaction either by metal ions or external bridging auxiliary ligands which produces two or three dimensional based network in ordered over interesting architecture [1,2]. Having multiple flexible phenyl groups attached to the porphyrin core facilitates various conformational changes and structural variability, which bring in different packing arrangements [3,4]. Which are bestowed by various non covalent interactions. In the past, extensive number of functionalizable porphyrin derivatives as building blocks for designing hydrogenbonded supramolecular networks have been reported [5]. Despite the above facts work on porphyrin based organic frame work has impetus significance over covalent organic framework, recently halogen bonded organic framework has been evolved; such interactions are mainly X-X, besides C-X-H, C-X- π . All though such covalent interactions are weak but provides excellent stability to crystalline lattices [5,6]. Above discussed interactions, in addition to electrostatics properties are essentially important part of quantitative descriptions that uses molecular electron density. But none of these can be better visualized and understood, which could be addressed by molecular electrostatic potential; (ESP) mapped on various molecular surfaces [7]. In this regards porphyrin can be evolved as special class as limited reports are presented, now it has got attention and reorganization which can be attempted to relate molecular surface ESPs, to crystal structure. In addition to ESPs calculations for deriving molecular and electrostatic parameters have been performed to supplement and rationalize the crystallographic results which include various packing motifs and intermolecular interactions predicating transformation and existence of hydrogen bonding interaction [8]. The current interests in the synthetic macrocycle had revealed a wide range of applications in diverse fields and got lot of attention. Diversities in their properties range from photovoltaic devices [9], data storage [10], photochemistry and photo physics [11], chemical sensors [12-14], semi conductors [15], catalysis [16], building block assemblies [1] etc. Several derivatives of porphyrin has been developed as photosensibilization agents; (PS) for photodynamic therapy; (PDT) [17]. In past several years self assembly has grown increasingly to develop advanced functional molecular material of improved diversely properties [18]. The main drive for this work was to get the detailed in-

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formation about geometrical disposition, intermolecular interaction and molecular three dimensional structural information which are responsible for crystal packing and utilization of such understanding in developing of new solids with desired physical and chemical properties. The x-ray crystal structure for the title compound has been first time reported and discussed in detail here. Furthermore supramolecular interaction observed was further quantified and analysis by HSA and 2D finger plotting which are discussed in detail in coming sections.

2. Experimental

2.1. Materials and methods

Chemicals employed for synthesis were commercially available. Analytical grades; (AR) chemicals were used for the synthesis without further purification. Solvents used for purification of chemicals were also of AR grade. Propionic acid, pyrrole, 4iodobenzaldehyde, chloroform and methanol were purchased from Sigma-Aldrich and were used without any further purification.

2.1.1. Analytical methods

FT-IR for H₂TIPP was registered between 400 cm⁻¹ to 4000 cm⁻¹ on Perkin Elmer Spectrum using KBr pellets. ¹HNMR spectra for the compounds were recorded on Bruker spectrometer, model AV 400 N (400 MHZ), using CDCl₃ as solvent and tetramethylsilane; (TMS) as internal reference. UV-visible spectra were obtained on Perin Elmier (Lamda 360) spectrophotometer in chloroform; (CHCl₃).

2.1.2. Synthetic procedure and crystallization of H2TIPP; [19]

Pyrrole (2.08ml, 20mmol) and 4-iodobenzaldehyde (3.65ml, 20mmol) were added to refluxing propionic acid (30ml) in a 100 ml round bottomed flask with constant stirring and was refluxed for half an hour at 80°C. The reaction mixture was allowed to cool at room temperature. The progress of reaction and purity was monitored by thin layer chromatography; (TLC). Shiny dark purple crude compound was then purified by column chromatography on silica gel using chloroform as the eluting solvent. The purified compound was recovered by the evaporation of the solvent under vacuum. The desired crystals of suitable size were obtained after repeated attempts at room temperature for x-ray diffraction by slow diffusion of n-hexane through dichloromethane solution.

H₂TIPP was obtained as Shiny dark purple crystals. Yield 0.38 g (21 %). Anal. data calc. for C₄₄H₂₆N₄I₄: C, 47.26; H, 2.34; N, 5.01, found: C, 47.23; H, 2.38; N, 5.06. FT-IR (KBr, cm⁻¹): ν (N-H) 3323, ν (C-H) 3084, ν (C-N) 1388, ν (C=C) 1559, ν (C=N) 1539, ν (C-H; β -pyrole) 972, ν (C-I) 1186. ¹H NMR (400 MHz, CDCl₃) δ : 8.88 (s, 8H, Porphyrin), 8.18 (d, 8H, Ph), 7.86 (d, 8H, Ph), -2.86 (s, 2H, NH_{imino}). UV-Vis [λ max (nm) in CHCl₃]: 421 (soret), 516, 551, 591, 647 (Q bands).

2.1.3. X-Ray crystallographic data collection and refinement of the structure

Shiny dark purple colour crystal of H₂TIPP having suitable size with approximate dimension of 0.218 × 0.166 × 0.113 mm³ was selected for X-ray diffraction measurement. The crystal was mounted under paratone oil and to get relative intensity data, the single crystal analysis was collected on a CCD Agilent SUPER-NOVA E (Dual) diffractometer using monochromated Cu-K α radiation (λ = 1.54184 Å) at 293(2) K. Using Olex2 [20], the structure was solved with the ShelXS [21], structure solution program using Direct Methods and refined with the ShelXL [22], refinement package using Least squares minimization. The positions of all the atoms were obtained by direct method. All non hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were refined with isotropic temperature factors, 1.2 U_{eq} of their parent atoms. The crystal was kept at 293(2) K during data collection. The crystal structure figures were generated by using Mercury software. Necessary crystallographic details of data collection and refinement are shown in Table 2.

2.1.4. Hirshfeld surface analysis

HSA has emerged as new and valuable tool to visualize various molecular interactions and has gained rapid popularity from last few years [23]. To redress and quantify various non covalent interaction we analyze crystal structures by HSA and 2D finger plots in addition to x-ray data generated by using Crystal explorer 3.1 [8,24], based on the interactions calculated from SC-XRD. The normalized function (d_{norm}) is ratio encompassing distance from HSA to nearest interior (d_i) and external (d_e) and the van der walls radii of atoms [25]. The red spots observed in HSA map generated with negative d_{norm} values considered to be close contact interactions which are quite responsible for molecular packing in crystal lattice. The white colour with zero d_{norm} is responsible for intermolecular distances, however the blue spots with positive d_{norm} represents the contacts which are longer than the sum of van der walls radii. Furthermore interaction energy were calculated by iso value of 0.02 au using wave functional calculations [26]. The method employed was B3LYP hybrid function and basic set 6-31G(d,p) for calculations. The 2D fingerprint plots were extended which could highlight particular atom pair contacts and enable the separation of contributions from different interaction types that overlap in the full fingerprint.

2.1.5. DFT methods

Theoretical calculation was carried out at the DFT level of theory, performed by using Gaussian 09 computational package [27]. The crystallographic information file; (CIF) of the title compound was used as input file for swotting their geometrical feature using density functional theory. Optimized geometry, electronic parameters were calculated by employing CAM-B3LYP basis functional in conjugation with 6-311G ++ (d, p) (for C, H, N) and LANL2DZ (for iodine atoms) basis sets [28].The absorption energies have been calculated with time-dependent density-functional theory; (TD-DFT) at the optimized geometries [29].

3. Results and discussion

H₂TIPP was prepared by the procedure reported using modified alder method [14]. Reaction scheme employed for synthesis is shown in Scheme 1. Reagents pyrrole and 4-iodobenzaldehyde were introduced simultaneously and were used in equimolar concentration to refluxing propionic acid, resulting in a colour change of reaction mixture to dark brown. Reaction mixture was allowed to stirrer for about 1 hour followed by a work up and washing with methanol and then by warm water. The crude compound obtained was subjected to column chromatography on silica gel with



Scheme 1. Synthetic reaction scheme.

Table 1

R	assignments	of	the	H2TIPP.
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Compound Functional group	H ₂ TIPP Experimental	Theoretical
v N-H (Stretching./ Bending) v =C-H (phenyl) v C=C/ C=N(asym/ sym.) v C-N v C-H (β-pyrole) v C-X	3323/ 965 3084-2850 1559, 1539, (1472/1466) 1346 972 1186	3536/ 984 3512-3400 1600,1592, (1488/1424) 1368 984 1184

chloroform as eluent and was dried on vacuum rotary evaporator resulting in the title compound. The compound was initially analyzed by Uv-visble, FT-IR, ¹H NMR to confirm the structure and purity of the compound. After which good quality crystal suitable for diffractions, was obtained after many repeated attempts by slow diffusion on n-hexane over dichloromethane as dark purple crystallite. The solid state SC-XRD helps us to unfold and enlighten the new iodo substituted porphyrin motif for effective supramolecular design in multi-dimensional array constructed by directional halogen bonded interaction. Additionally manifestation of molecular interactions and their influence on morphology were established and supported by HSA and 2D finger prints.

FT-IR spectra both (experimental and theoretical) presents characteristic IR bands of the H_2 TIPP are presented in (Fig. S1-S2 ESI[†]). A band characteristic among all free base porphyrins appearing at 3323 cm⁻¹ was assigned to N-H stretching vibrations and bending vibrations at 965 cm⁻¹, which are in close approximation with relative series of halogen derivatives having average value of ~3300(± 25) and 965(± 5) cm⁻¹ respectively. Other intense sharp spike in the range of 3084-2850 cm^{-1} corresponding to aromatic v_{C-H} stretching frequency. v(C=C/C=N) appears in the range of ~1559 cm⁻¹ to ~1472 cm⁻¹. ν C-H (β -pyrole) was assigned stretching frequency of 972 cm⁻¹ with increase in frequency by (± 12) cm⁻¹ to that of calculated results. Similarly v_{C-N} frequency was observed at 1346 cm⁻¹. The important v_{C-X} functional group in halogen series was assigned stretching frequency of 1089 cm⁻¹ respectively [14]. However theoretical IR show mainly similar peaks having relatively higher values for characteristic functional groups.

Calculated IR results are in agreement with the experimental values and are summarized in Table 1 [30]. ¹H NMR convenient technique for identification of porphyrin compound was recorded at room temperature in CDCl₃ using TMS as internal standard, The complete spectra are presented in supplementary file (Fig. S3 ESI[†]). The signal associated to NH protons resonates at $\sim \delta$ = 2.86 ppm as low intensity singlet which are highly shielded due to anisotropic effect of aromatic ring current, characteristic among all meso-porphyrin derivatives and are in consonant with the literature data [31]. While *meso* and β -pyrrole protons are highly deshielded and further facilitates the identification. β -pyrrole protons represented by (H_a) resonates as singlet's at $-\delta = 8.88$ ppm. However a meso-aryl proton (Hb) and (Hc) assigned at $\sim \delta$ 8.18 and 7.86 ppm. Uv-vis absorption spectra (theoretical and experimental) were recorded in chloroform represented in (Fig. S4-S5 ESI†). As reported characteristic of porphyrin derivatives, H₂TIPP too featured two prominent absorption bands (B or soret and Q band) arises from $\pi \rightarrow \pi^*$ transition. A high intensity B band appearing at λ_{max} 421 nm corresponds to strongly allowed transition from $S0 \rightarrow S2$ state and lower intensity Q-bands distributed among four bands in visible range appears in rage of λ_{max} 516-647 nm attributed to weakly allowed electronic transition from $S0 \rightarrow S1$ state respectively. Obtained theoretical Uv-visible spectra demonstrate similar absorption bands. Soret band appears with maximum absorption showing sharp shift by (\pm 75 nm) appearing at around λ_{max} 337 nm, however Q bands split as single broad band within the range of λ_{max} 504-512 nm respectively [32].

3.1. Single crystal X-ray diffraction studies

Ortep plot for H₂TIPP; ($C_{22}H_{13}I_2N_2$) presented in Fig. 1a with necessary crystallographic data and structure refinement in Table 2. The title compound crystallizes in triclinic, space group P-1 having unit cell dimensions a = 6.5175(4) Å, b = 13.3470(9) Å, c = 14.2984(13) Å, $\alpha = 116.190(8)^\circ$, $\beta = 98.838(6)^\circ$, $\gamma = 93.157(5)^\circ$, V = 1092.21(14) Å³, Z = 2, occupying 4 independent molecules per unit cell, extend as 3D and 2D supramolecular architecture represented in Fig. 2. The asymmetric unit posse's half porphyrin molecule containing two pyrrole rings one with secondary amino nitrogen and other by imino nitrogen atom. The two pyrrole aro-



Fig. 1. (a) ORTEP plot, the ellipsoids were drawn with 50 % probability (b) Optimized structure for H₂TIPP

Table 2 Crystal data and structure refineme	ent for H ₂ TIPP
Crystal data and structure refinemed Identification code Empirical formula Formula weight Temperature/K Crystal system Space group a/Å b/Å c/Å $\alpha/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ Volume/Å ³ Z $\rho_{calc}g/cm^{3}$ μ/mm^{-1} F(000) Crystal size/mm ³ Radiation 2 Θ range for data collection/° Index ranges Reflections collected Independent reflections Data/restraints/parameters Coodness.of. ft on E ²	$\begin{array}{l} & \text{H}_2\text{TIPP} \\ & \text{H}_2\text{TIPP} \\ & \text{C}_{22}\text{H}_{13}\text{L}_{2}\text{N}_{2} \\ & 559.14 \\ & 293(2) \\ & \text{Triclinic} \\ & \text{P}-1 \\ & 6.5175(4) \\ & 13.3470(9) \\ & 14.2984(13) \\ & 116.190(8) \\ & 98.838(6) \\ & 93.157(5) \\ & 1092.21(14) \\ & 2 \\ & 1.700 \\ & 22.657 \\ & 530.0 \\ & 0.218 \times 0.166 \times 0.113 \\ & \text{CuKa} (\lambda = 1.54184) \\ & 7.02 \text{ to } 133.8 \\ & -5 \le h \le 7, -15 \le k \le 15, -17 \le l \le 15 \\ & 6283 \\ & 3835 \ [\text{R}_{int} = 0.0295, \text{R}_{sigma} = 0.0394] \\ & 3835/0(235) \\ & 1.082 \end{array}$
Final R indexes [I>=2 σ (I)] Final R indexes [all data] Largest diff. peak/hole / e Å ⁻³	$\begin{array}{l} 1.082 \\ R_1 = 0.0691, \ wR_2 = 0.2142 \\ R_1 = 0.0776, \ wR_2 = 0.2312 \\ 2.88/-0.93 \end{array}$

matic rings are linked to each other through a methyldine (mesocarbon) bridge by α positions and two para iodo substituted phenyl rings which are linked to meso carbon atom. Further expanded by symmetry operations (-x, -y, -z). The porphyrin core possessing 24 atom with N(1) and N(2) atoms defining the N_4 core, which is ideally planer having some distortion. On the other hand four phenyl rings are distorted out of the plane of core (Fig. S6 ESI[†]). The possibility of deviation from planarity seems to be due to the steric crowding arising from neighboring phenyl and H atoms from the pyrrole, and other neighbouring close contacts. N(1) and N(2) atoms posses two distinct imino and amino pyrrole moieties which are non equivalent showing torsion angle of 4.1 (14) and 8.0 (13)° for iodo and 5.01/ 6.2, 10.75/ 4.03 for Cl and Br derivative respectively. Inner NH groups of porphyrin core are involved in intramolecular bifurcation of N(1)-H(2)•••(N,N) hydrogen bonds resulting in formation of semi-quasi six membered rings at opposite face. The average interatomic distance of C-N was calculated to be $1.35(\pm 0.2)$ Å and C-Br was (2.100 and 2.111 Å) for two differently oriented meso-iodo substituted ends, which are similar to those of porphyrin-halogen based molecules. The two opposite trans amino pyrrole rings are alternately tilted above and below the plane of the porphyrin macrocycle, thereby reducing the transannular interactions. The trans annular separation for N-H hydrogen atom calculated and was found to be 2.41Å for H₂TIPP, However for Cl, Br derivative it was found to be 2.43 and 2.41 Å [31,33]. Selected bond distances, angles and torsion angles are listed in (Table S3-S5 in ESI†).

3.1.1. Supramolecular interactions

The crystal packing seems to be controlled by various intra, intermolecular hydrogen bonding and other neighboring contacts. The prominent intramolecular hydrogen bonding appears by inner NH group via. N-H•••N. The packing is further stabilized by H-H. C-H interactions besides other neighboring contacts [31,33]. Hydrogen bonding and other important close interactions are listed in Table 3-4. From packing diagram one can visualize that 4 molecule are occupying edge position with 2 independent molecules stacked exactly one above the other in slightly off set/ slipped manner (type alignment) which are very much parallel to the other porphyrin derivatives reported [6,33]. The stacking is either from N-H••• π , C-H••• π and π ••• π . However the two stacking pairs are interconnected by C-H•••C or C-I••• π (Fig. 3). π ••• π interaction, between closet atom-atom distance was calculated 3.843 Å. The molecule is further connected by most prominent I•••I interaction separating them by 3.95Å which are week but quite useful among stability of crystal lattice (Fig. S7 ESI[†]). Close contacts involving neighboring atoms can visualized from (Fig. S8 ESI[†]).

Furthermore 2D structural motifs of porphyrin framework showing interporphyrin voids for bromo and iodo derivative in halogen substituted porphyrin series represented in Fig. 4. These building blocks are oriented in a linear fashion and break them into a continuous hexagonal channels indicating to be porous solids.

3.1.2. Hirshfeld surface analysis

The standard resolution HSA attributes various intermolecular interactions in crystal system associated with finger print plots to the indirect approximation from x-ray diffraction providing deeper and additional insight in the crystal which is otherwise difficult to gauge by standard techniques. To quantify such interactions we predetermine supramolecular interaction by HSA and 2D mapping in addition to crystallographic data for H₂TIPP and their corresponding (Cl, Br) derivatives. In addition energy frame work calculations between pairs of molecules for intermolecular interaction in molecular crystal were extended to whole series. Although Cl and Br derivative have been characterized by structural analysis previously but ESP for Cl and molecular interaction energy for both porphyrin derivative has not been addressed. HS of the



Fig. 2. (a) 3D supramolecular architecture formed due to hydrogen bonding interaction and (b) 2D layers using integrated packing along b-axis

Table 3

Comparative analysis of potential hydrogen bonds of H₂TIPP with other halogen; (X=Cl, Br) substituted porphyrin derivatives.

Sample Codes	D-H•••A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D- H•••A /°	Ref.
H ₂ TClPP	$N(2)-H(2) \bullet \bullet N(1)^{a}$	0.861	2.364	2.903	121.01	[6]
	$N(2)-H(2) \bullet \bullet N(1)^{a}$	0.861	2.364	2.923	120.53	
H ₂ TBrPP	$N(2)-H(2) \bullet \bullet N(1)^{a}$	0.880	2.360	2.910(3)	120.8	[33]
	$C(12)-H(12) \bullet \bullet N(1)^{b}$	0.950	2.599	3.384(4)	140.2	
	$C(16)-H(16)-Br(1)^{b}$	0.950	3.170	3.742(3)	120.5	
H ₂ TIPP	$N(2)-H(2) \bullet \bullet N(1)^{a}$	0.860	2.340	2.884(9)	121.2	This Work
	C(22)-H(22)•••N(1) ^b	0.930	2.688	3.618(8)	136.40	
	C(8)-H(1)•●●C(20) ^b	2.100	3.629	5.729(9)	164.85	
	$C(8)-I(1) \bullet \bullet \bullet C(20)^{b}$	2.100	3.629	5.729(9)	164.07	

Symmetry operators: (i) x, y, z (ii) -x, -y, -z. a intramolecular H-bonding

b neighbouring contacts.



Fig. 3. Stacking responsible for stability of crystal lattice by (a) Coool, Coool and (b) Noool, Coool interactions.



Fig. 4. Interporphyrin voids in (a) H₂TBrPP and (b) H₂TIPP.

 Table 4

 Stacking interactions calculated in (Å) determined by X-ray diffraction.

N-H••• <i>π</i>	С-Н•••π	π •••π
2.689/0.930	2.855/0.930	3.843

H₂TXPP; (X=Cl, Br and I) series have been mapped with (d_{norm}) shape index, and curvedness presented in Fig. 5. The d_{norm} value is mapped onto the hirshfeld surface by red, white or blue color. The red regions represent closer contacts with a negative d_{norm} value, whereas the blue regions represent longer contacts with a positive d_{norm} value. Moreover, the white regions represent the distance of contacts equal to the van der waals separation and have a d_{norm} value of zero. The surfaces were shown to be transparent to make the molecular moiety could be visualized of various supramolecular interaction, around which they were calculated. HS show many red spots of varying intensities and strengths. One such intense red spot appears to be NeveH close contact of 2.68

Å appearing from imino nitrogen and hydrogen atoms of neighboring mesophenyl group Fig. 6a. Other intense red spot is observed which corresponds to Coool interaction of 2.10 Å appearing between peripheral halogen atoms with the carbon possessing iodine atom Fig. 6b. For Cl and Br derivative the most important interactions appears from H•••C, C•••C and N•••H, H•••Br Hood [31,33]. These described interactions involve higher stability of crystal packing which inturn project these compounds for diverse application in solid state. Above stated interaction featuring spikes of various lengths and thickness can be contrasted by the 2D finger plots represented in Fig. 7. The 2D fingerprint plots could highlight particular atom pair contacts and enable the separation of contributions from different interaction types that overlap in the full fingerprint. Using the standard 1.0 - 2.8 views with the d_e and d_i distance scales displayed on the graph axes. The most dominant close contact interaction is H ++++ H intermolecular contact contributing about 40.7 % for iodo and 36.3, 40.1 for Cl and Br derivative to that of total HS. However most relevant interactions which are responsible for crystal packing are C•••H, C••• and NoooH contributing 15.1, 8.8, and 3.1 % for title compound. In



Fig. 5. HS mapped with d_{norm} , shape index and curvedness plots for H₂TXPP series (red: negative, white: zero, blue: positive).



Fig. 6. Hirshfeld surface mapped with dnorm ranging from -0.4 Å (red) to 3.11 Å showing close contacts with neighboring molecules; (a) N•••H (2.68 Å) and (b) I•••C (2.10 Å).

addition the existence of $\pi \cdots \pi$ stacking in Br and I derivative are dominant over chloro derivative. X $\cdots X$ interactions are very much evident with de + di \approx 3.95 Å with contribution of about 3.9, 1.5 and 1.9 % respectively. Percentage contributions of individual intermolecular interaction on the basis of hirshfeld surface analysis are shown in bar graph in Fig. 8. Above discussed supramolecular interactions are in close agreement with other porphyrin derivatives [5]. Calculation for intermolecular interaction energy was performed at B3YLP/6-31G(d,p) model for energy frame work analysis. A cluster of 3.8 Å was generated round the selected fragment and energy was calculated applying symmetry operation with respect to the central molecule. The distribution of the interaction energy as $E_{tot} = k_{ele}E'_{ele} + k_{pol}E'_{pol} + k_{dis}E'_{dis} + k_{rep}E'_{rep}$ where as (K represents scale factor, E'_{ele} = electrostatic component; E'_{pol} = polarization energy, E'_{dis} = dispersion energy and E'_{rep} = exchange repulsion energy). Table 5 represents numerical values for interaction energy in (kJ/ mol) and scale factor for B3YLP/6-31G(d,p) model energies in Table 6. Net interaction energy calculated for pair wise molecular interaction construction for frameworks were evaluated [34]. The overall interaction energy are electrostatic (-9.3/-40.1/-51.2 kJ mol⁻¹), polarization (-6.5/-16.2/-14. 2 kJ mol⁻¹), dispersion (-126.9/-289.6/-290.6 kJ mol⁻¹), repulsion (53.2/162.8/154.2 kJ



Fig. 7. The 2D fingerprint plots with *di* and *de* ranging from 1.0 to 2.4 Å for H₂TXPP series



Fig. 8. Percentage contribution of individual intermolecular interaction on the basis of hirshfeld surface analysis.

 mol^{-1}) and total interaction energy (-85.2/-198.3/ 198.3 kJ mol^{-1}) for Cl, Br and Iodo derivatives.

3.1.3. DFT calculation's

Optimized geometry from density functional theory for H₂TIPP is presented in Fig 1(b) involving N-H•••H intra-molecular hydrogen bonding within the core therein. Geometrical parameters both (experimental and theoretical) with selected bond length and bond angles are listed in (Table S3-S5 ESI†). Calculated geometrical parameters found are in good agreement with experimental values obtained from x-ray diffraction data. Slight deviation observed can be attributed to the fact that the theoretical calculations were carried in a gas phase for single isolated molecule, however the experimental values were obtained in crystalline solid phase. The optimised geometry of iodine substituted tetraphenylporphyrin; TPP display that the core framework including the pyrrole rings and meso-carbon junction opts a planar geometry. However the peripheral phenyl rings containing iodine substituents are twisted from that core plane approximately perpendicular to each other can be visualized as a slightly distorted propeller. Both theoretical and experimental geometries evidences strong hydrogen bonding between amino (N-H) hydrogen and inner core imino (N) atom displaying a strong essence of a quasi-aromatic six member rings at two opposite ends. This result in cancelling the dipole moment to zero, however the net dipole moment was found to be 0.0001μ . That could be attributed to the peripheral polarisable iodine atom. The components and energies of the frontier molecular orbital's; (FMOs) provide better insight in chare transfer transitions proper-

Table 5

Energies in i	kj moi	· IOF H ₂ IXPP -series.						
H ₂ TClPP	Ν	Sym	R	E_ele	E_pol	E_dis	E_rep	E_tot
	4	-x+1/2, y+1/2, -z+1/2	13.36	-3.8	-1.6	-28.1	9.6	-22.5
	2	x, y, z	13.56	3.1	-1.5	-35.0	13.3	-18.6
	4	-x1/2, y+1/2, -z+1/2	11.51	-7.3	-3.2	-55.9	23.1	-41.2
	4	-x+1/2, y+1/2, -z+1/2	18.44	-1.3	-0.4	-7.9	7.2	-2.9
H ₂ TBrPP	2	х, у, z	6.18	-19.3	-10.7	-164.8	74.0	-115.1
	4	-x, y, -z+1/2	14.55	-3.3	-1.3	-27.5	19.3	-13.3
	2	-x, y, -z+1/2	13.17	0.4	-1.9	-60.2	31.9	-29.2
	2	x+1/2, y+1/2, z	13.86	-13.2	-1.6	-27.3	21.7	-21.4
	4	-x+1/2, y+1/2, -z+1/2	14.57	-1.4	-0.3	-9.4	3.4	-7.4
	2	x+1/2, y+1/2, z	16.39	-3.3	-0.4	-20.4	12.5	-11.9
H_2TIPP	1	х, у, z	6.52	-18.8	-9.4	-151.9	63.1	-111.0
	1	х, у, z	13.35	-2.4	-1.8	-60.3	27.9	-35.4
	0	х, у, z	14.30	-10.6	-1.1	-26.4	17.3	-21.3
	1	х, у, z	15.17	-19.4	-1.9	-52.0	45.9	-30.6

N refers to number of molecules with an R molecular centriod to centriod distances in Å.



Fig. 9. Frontier molecular orbitals; (FMOs) of H₂TIPP calculated at CAM-B3LYP level of theory.

Table 6

Casla Fasta		ala V		IZ	IZ
gies with B3I	LYP/6-3	81G(d,p) n	nonome	r electr	on densities
Scale factor a	and fit	statistics	for CE-	B3LYP	model ener-

Scale Factor	K_ele	K_pol	K_disp	K_rep
	1.057	0.740	0.871	0.618

ties. A concise illustration of the frontier orbital's of the H_2 TIPP in neutral state are a shown in (Fig. 9). It was observed that the highest occupied molecular orbital; (HOMO) of the molecules delocalize primarily over the pyrrole ring, with a major contribution nitrogen atoms and minor contributions from the substituents phenyl rings whereas the lowest unoccupied molecular orbital; (LUMO) localize largely pyrrole rings and meso-links and with no contributions from the substituents phenyl rings. Thus, the first excitation will originate from HOMO orbital's including $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ transitions. Frontier molecular energies were found to be, for $E_{\rm HOMO}$ = - 4.680 eV and E _{LUMO} = -0.1791eV, its observed that HOMO-LUMO gap $\Delta E_{\rm (H-L)}$ of the title compound decreases as com-

Compound	Energy (cm ⁻¹)	Wavelength (nm)	Osc. Strength (a.u.)	Orbital contribution %
H ₂ TIPP	19530.850	512.01	0.1365	H-1→L+1 (31%), HOMO→LUMO (67%
	19836.536	504.12	0.0054	H-1→LUMO (42%), HOMO →L+1 (56%)
	29597.525	337.86	1.2899	H-1 \rightarrow LUMO (58%), HOMO \rightarrow L+1 (42%)

pared to that of unsubstituted TPP and was found to be 4.5009 eV. The H₂TIPP displays higher values of IP due to presence of more electronegative iodine atom. By combining relationships between IP values and presence of low lying HOMO and LUMO energy level signifies that the studied systems possess high oxidation and reduction stabilities. The calculated polarizability α (x 10^{- 24}esu.) was found to be 566.40 au.

Furthermore we employed TD-DFT studies at CAM-B3LYP level of theory to understand the electronic absorption behavior in gas phase as well as in solvent using PCM model. The calculated energies, wavelength (λ_{max}), oscillator strength and orbital contribution for H₂TIPP are presented in (Table 7). The calculated values reveal that in absorption spectra of H₂TIPP displays a strong absorption peak between $\lambda_{max} = 512$ nm originates from HOMO to LUMO transition with contribution of about 67%. This could be attributed to $n \rightarrow \pi^*$ transitions originates from macrocyclic porphyrin ring [35].

4. Conclusion

Detailed structural description, comparison and study of various supramolecular interactions associated with H₂TIPP were addressed first time by single crystal x-ray diffraction studies, in combination with computational analysis apart from analytical characterizations. Our results displays strong interplay of intramolecular hydrogen bonding occurring from N-H•••N, and other neighboring contacts H•••H, C•••H, I•••I. Stacking pairs are interconnected by C-H•••C, C-I••• π and π ••• π which further involves in stabilising their crystal packing. These stated interaction orient them in multi-dimensional supramolecular building blocks, indicated their greater role as porous materials. These structural features has been further quantified and confirmed by HSA, and 2D finger plotting. Finally interaction energy analysis confirms dispersion of supramolecular network involving in stabilization were calculated.

Supporting information available

Charcaterization details, crystal data parameters, aditional figures are attached with supplementary file. Additional crystallographic data have been provided and deposited as (supplementary data) with the Cambridge crystallographic data centre and may be obtained on request quoting the deposition number CCDC 2023758 for H2TIPP from the CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; E-mail address:deposit@ccdc.cam.ac.uk).

Declaration of Competing Interest

Authors declare no competing financial interest or any personal issues.

CRediT authorship contribution statement

Umar Ali Dar: Conceptualization, Visualization, Investigation, Writing - original draft, Writing - review & editing. **Shakeel A. Shah:** Supervision.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130601.

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