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Halogen Bonded Assemblies of Arylene-imides and -diimides: Insight from Electronic, Structural and Computational studies

Kalyanashis Mandal,^[a] Deepak Bansal,^[b] Yogendra Kumar,^[a] Rustam,^[a] Jyoti Shukla^[a] and Pritam Mukhopadhyay^{*[a]}

Abstract: Halogen bonding interactions in electron deficient π scaffolds has largely been underexplored. Herein, we have studied the halogen bonding properties of arylene-imide/-diimide-based electron deficient scaffolds. We probed the influence of: scaffold size, small phthalimide (PTMI), e.a. from moderately-sized pyromelliticdiimide (PMDI) or naphthalenediimides (NDIs) to large perylenediimide (PDI); axial-group modifications; varied number of halogens, etc. on the halogen bonding and its self-assembly in a set of nine molecules. The structural modification leads to tunable optical as well as redox property. The first reduction potential, E¹_{1/2} range between -1.09 to -0.17 V (vs SCE). Two of the molecules, e.g. 6 and 9 embrace deep-lying LUMOs with values reaching -4.2 eV. Gratifyingly, we realized single crystals of all the nine systems, which revealed Br...O, Br...Br or Br... π halogen bonding interactions, with few systems capable of forming all the three-types. These interactions lead to halogen bonded rings (up to 12-membered), which propagate to form stacked 1D-, 2D- or corrugated sheets. We also identified few outliers, e.g. molecule which prefer C-H-O hydrogen bonding over halogen bonding; or a non-centrosymmetric organization over the centrosymmetric ones. Computational studies based on Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) analysis provided further insight into the halogen bonding interactions. This study can lead to a predictive design tool-box to further explore related systems on surfaces reinforced by these weak directional forces.

Introduction

Halogen bonding (XB) has gained widespread importance as a non-covalent interaction as it manifests multitude of interesting physico-chemical properties.^[1] These interactions have been widely exploited in the solid state for manipulating electronic, magnetic, nonlinear optical properties, crystal-to-crystal conversion, and recently for chiral information transfer.^[2] Halogen bonding can also modulate electron deficiency of the π -scaffolds with electron mobility (μ_e) reaching up to 8.6 cm² V⁻¹ s⁻¹.^[3] Whereas, in solution phase, effect of halogen bonding interactions have been utilized in understanding cation or anion binding interactions, anion transport, drug designing, etc.^[4]

[a] Dr. K. Mandal, Dr. J. Shukla, Dr. Y. Kumar, Mr. Rustam, and Dr. P. Mukhopadhyay Supramolecular and Material Chemistry Lab, School of physical sciences, Jawaharlal Nehru University, Delhi -110067, India. E-mail: m_pritam@mail.jnu.ac.in
[b] Dr. D. Bansal Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden – Germany. Supporting information for this article is given via a link at the end of the document. Nowadays, halogen bonding interactions are fast emerging as an efficient alternative to hydrogen bonding (HB) interactions.^[1,5] In contrast to a HB, halogen bond constitutes a covalently linked electron rich halogen atom directionally interacting with electron rich nucleophilic species such as anion/lone pairs. Such unique mode of interaction is conceivable by the presence of positive region on halogen atom, conceptualized as σ -hole by Politzer in 2007.^[6] In the last two decades, there have been a persistent effort by several research groups to rationalize this enigmatic nature of halogen bonding. In 2003, Resnati and coworkers reported halogen bonded architecture comprising of Br...Novridvl interaction,^[7] while, in 2004, Bruce and coworkers reported formation of liquid crystals with a halogen bond.^[8] In 2007, Zou and coworkers theoretically proved the biologically relevant Br...Ophosphate interaction between adenine-5-bromouracil and organic phosphate ion.^[9] Findings by the Diederich^[10] and Parish^[11] groups demonstrated the biological significance of halogen bonding in proteins and DNA. Interestingly, Rissanen^[4b] and Diederich^[12] have independently demonstrated construction of supramolecular cages using halogen bond interaction. A recent work from the Beer's group demonstrated the importance of halogen bonding in anion recognition by a chiral [2]rotaxane.^[12] In addition, presence of halogen atoms on the periphery of organic/inorganic synthons has attracted scientific community to augment the construction of supramolecular self-assemblies.^[13] Very recently, Molina and co-workers reported the generation of interlocked supramolecular polymers assisted by halogen bonding.^[14] Bowling and coworkers reported the stabilization of a triangular system via halogen bond interaction where rigidity of halogen bond bridge depends upon the nature of donor halogen atoms as well as the acceptor carbonyl groups.^[15] Therefore, the strength of halogen bonds can be fine-tuned by varying the motif covalently bound to halogen atom.

In this context, inherently electron deficient aryleneimides/ arylenediimides π -scaffolds (naphthalenediimides: NDIs and perylenediimides: PDIs)^[16] provide promising platform towards the rational synthesis of halogen bonded self-assemblies. Moreover, these scaffolds are envisaged to hold significant number of directionally aligned halogen atoms which can have important ramifications in the formation of halogen bonded architectures and their opto-electronic properties. A preliminary investigation towards this effort was done by our group with the PDI scaffold.^[3b] Recently, the Gade group demonstrated twisting of the π -rings in tetraazaperopyrenes (TAPP) by varying number of halogen atoms.^[3c,d] However, there are no systematic studies till date, which delineates the effect of the size of the aryleneimide/-diimide π -scaffolds, changes in its constituent atoms, its number and the peripheral substituents on the halogen bonding.

Herein, we have studied the halogen bonding properties of diverse range of di-, tetra- and octa-brominated arylene-imide/diimide-based systems (Schemes 1-2). We have explored the

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size influence of: a) scaffold (phthalimide: PTMI, PMDI, pyromelliticdiimide: naphthalenediimide: NDI and perylenediimide: PDI), b) axial-group modifications (imide N-R: R = H; n-Butyl; n-Hexyl; Mesityl), c) varying the number of halogens, d) H atoms in combination with the halogen atoms, and e) imide carbonyl oxygen atom versus sulfur atoms, on the halogen bonding and its self-assembly. The molecules revealed presence of two type of halogen bonding interactions: i) Br...Br and ii) Br. Oimide. Computational studies were performed to identify the electronic and energy density functions of the halogen bonding interactions using AIM analysis and extent of the orbital overlaps by NBO analysis and their interactions by Hirshfeld crystal surface analysis.



Scheme 1. Top: General schematic representation of intermolecular halogen bonding interaction (X = Br and Y = Br/O). Bottom: Variations engineered through: π -scaffold size, axial groups, imide (C=O/C=S) groups and variation of no. of halogen atoms.



Scheme 2. Molecular structures of 1-9.

Results and Discussion

Halogenation and perhalogenation of electron deficient π -scaffolds entail major synthetic drawbacks such as use of hazardous and corrosive molecular bromine, high temperatures, and low yields.^[17-20] We have exploited effective synthetic pathways by reacting commercially available and economically

viable 1,3-Dibromo-5,5-dimethylhydantoin (DBH) as a source of bromine with different starting materials to afford various di- and tetra-bromo substituted precursors. These precursors were further treated with the respective amines either in acetic acid or DCM-PBr₃ mixture to obtain different class of di-, terta- and octabromo substituted imidized products such as PTMI, PMDI, NDI and PDI (Scheme 2). Applying DBH as a brominating reagent all the compounds were synthesized in good yields and characterized using different analytical techniques such as FTIR, UV-Vis, NMR and Mass spectroscopy (Figures S1-S16; ESI).

Interestingly, FTIR spectra also suggests the influence of molecular modulation as well as potential intra- or inter-molecular Br···O_{imide} interactions on the C=O stretching frequency ($\nu_{c=0}$) of the molecules (Figure S17; ESI). Notably, $v_{c=0}$ stretches for the brominated imides were observed in the range between 1563 cm⁻ ¹ to 1771 cm⁻¹. To our observation, **1** exhibit single $v_{c=0}$ stretch at 1688 cm⁻¹ whereas its diimide counterpart **2**, exhibit two $v_{c=0}$ stretches at higher energy of 1771 cm⁻¹ and 1705 cm⁻¹. This is in accordance with the crystal structure which reveals the presence of two unequal intra-molecular Br···Oimide interaction in 2 (3.199 Å and 3.238 Å) resulting in the appearance $v_{c=0}$ stretches at two different positions. Similarly, tetra bromo NDIs 7 and 8 also exhibit two $v_{c=0}$ stretches due to the presence of two different intramolecular Br...Oimide interactions. On the other hand, considerable influence of inter-molecular Br...Oimide interaction is observed in the structurally comparable dibromo NDIs 3-6. While taking 3 as a reference where the inter-molecular Br...Oimide is 3.256 Å and its C=O group stretches at 1671 cm⁻¹ and 1563 cm⁻¹. The intermolecular Br...Oimide separation in 4 increased to 3.736 Å resulting in the appearance of $\nu_{c=o}$ stretches at 1705 cm⁻¹ and 1647 cm⁻¹. Similarly, comparison of inter-molecular Br···O_{imide} interaction in 3 with 5 (3.513 Å) also exhibits increase in C=O stretching frequency to 1721 cm⁻¹ and 1671 cm⁻¹. Understandably, increased inter molecular separation leads to dimmining of C=O interaction with other molecule(s) thus having more of double bond character and therefore higher stretching frequency. However, ${\bf 6}$ exhibit closer Br…O_{imide} separation of 3.175 Å to ${\bf 3}$ which corroborates with the comparable $v_{c=0}$ stretching of 1688 cm⁻¹ in 6. These observations suggest the potential influence of intermolecular XB interaction on electronic properties of the molecules.

The absorption spectra of the compounds were recorded in DCM to understand the influence of π -scaffold size, axial and core modulation on the UV-vis profile (Figure 1). However, due to poor solubility of **3** in DCM, its spectrum was analyzed in DMF. Notably, all the compounds, except **6** and **9**, exhibited predominant π - π * absorption features within the range of 330-450 nm (Table 1). Interestingly, while tetrabromo-phthalimide (1) exhibit sharp π - π * responses at 330 nm and 340 nm, dibromo-PMDI (**2**) exhibits similar absorption features red-shifted by ca. 20 nm. Moreover, in dibromo-NDI (**3**) both these absorption features were further red-shifted by ca. 10 and 40 nm, respectively. Such observations suggest decrease in π - π * energy gap with increased electronic delocalization.



Figure 1. Absorption spectra of 1, 2, 4-9 (0.3 μ M) in DCM, 3 (0.3 μ M) in DMF.

Furthermore, the axial group(s) modification in the NDI display weak electronic influence on its absorption profile. For example, in 3, having only hydrogen at the axial position, displays band at 360 nm along with a shoulder at ca. 400 nm, while, these bands were found at similar positions in 4 and 5 substituted with axial nhexyl chain and aromatic mesityl group, respectively (see table 1). In contrast, replacement of the two diagonally opposite O atoms of the carbonyl groups in 5 with sulphur atoms (6) induces significant effect on the electronic transitions with absorption bands at 486 and 513 nm, which is red-shifted by ca. 120 nm and 100 nm compared to corresponding bands in 5. Moreover, tetrabromo-NDIs 7 and 8, being analogous counterparts of dibromo-NDIs 4 and 5, displayed π - π * absorption peaks red shifted by ca. 40 nm and 20 nm, respectively. Furthermore, increased aromaticity as well as perbromination in octabromo-PDI **9** exhibits highly red-shifted absorption spectrum. Interestingly, solid state absorption of all the compounds were recorded to identify the presence of potential H-type or J-type stacking (Figure 2). Interestingly, in case of compounds 1, 3 and 4, the absorption bands are blue-shifted by ca. 8 nm, 35 nm and 15 nm, respectively. These blue shifted values indicate their potential to form H-aggregates (Table 1). While, the compounds 5, 6, 8 and 9 showed red-shifted absorption in their solid-state, indicating Jtype stacking interactions. These observations are supported by the solid-state packing of the molecules. For example, while molecules 1, 3 and 4 were observed stacked parallel to each other via π - π interaction, the others show more of a slipped or off-set π - π stacking interactions.



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Table 1. Absorption data in solution and solid-state 1-9. Malagula 1 Malagula 1 Malagula 1 Malagula 1]
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Molecule $\Lambda_{\max(sol)}$ [nm] ϵ_{sol} [N1 ^{-e} m ⁻¹] (X10 ⁻) $\Lambda_{\max(solid)}$ [nm	
1 331, 340 0.29, 0.30 332	
2 350, 365 0.46, 0.51 365	
3 361, 400 1.68, 0.35 365	
4 362, 405 1.31, 0.86 347, 416	
5 362, 405 1.95, 0.12 365, 410	
6 486, 513 0.84, 0.82 485, 515	
7 398, 424 1.25, 1.21 427	
8 396, 425 0.81, 0.73 427	
9 470, 536 1.59, 1.97 477, 550	

Electrochemical Studies

Next, we determined the redox properties of compounds 1-9 by performing cyclic voltammetry studies (Figure 3, Tables 2). Most of the compounds exhibited highly reversible redox response(s) toward the negative potential of the voltammogram. Interestingly, electrochemical studies could explicitly differentiate between the structural modulations in terms of the nature of the π -scaffold, axial- and core-substitution in these compounds. For examples, while 1 exhibits single quasi-reversible redox response at $E_{1/2}$ = -1.09 V having peak to peak separation of 103 mV (ΔE_{ρ}), its diimide counterpart, 2, exhibits a reversible redox signal at $E_{1/2}$ = -0.68 V $(\Delta E_p = 72 \text{ mV})$ comparatively shifted by 410 mV towards positive potential. Moreover, in case of the axial-modified NDIs 3-5, no considerable electronic influence was observed. In case of 3, napthalenediimide exhibits two redox waves at $E^{1}_{1/2} = -0.47$ ($\Delta E_{p} =$ 105 mV) and $E^{2}_{1/2}$ = -0.90 V (ΔE_{p} = 140 mV). Whereas in **4**, both these redox waves were observed at $E_{1/2}^{1} = -0.49 \text{ V} (\Delta E_{\rho} = 66 \text{ mV})$ and $E^2_{1/2}$ = -0.95 V (ΔE_p = 67 mV). Moreover, these redox potentials were found to be at $E_{1/2}^{1} = -0.44 \text{ V} (\Delta E_{p} = 61 \text{ mV})$ and $E^{2}_{1/2}$ = -0.91 V (ΔE_{p} = 72 mV) in case of 5. These values suggest that redox potential remain negligibly shifted by ca. $\pm 0.02 \text{ V} (E_{1/2}^{1})$ and ca. $\pm 0.04 \text{ V}$ ($E^{2}_{1/2}$) on changing the axial groups. Interestingly, such observations corroborate our findings in absorption studies toward the negligible influence of axial modification on the electronic properties of these compounds, as expected for lack of electronic communication between the pendant axial groups and the π -scaffold. However, in case of **6**, considerable shift towards less negative potentials at $E_{1/2}^{1}$ = -0.20 V (ΔE_{p} = 79 mV) and $E_{1/2}^{2}$ = -0.56 V (ΔE_{ρ} = 79 mV) was observed. Moreover, in case of tetrabromoNDIs 7 and 8, both exhibits two reversible redox responses at $E_{1/2}^{1}$ = - 0.38 V (ΔE_{ρ} = 59 mV) and $E_{1/2}^{2}$ = - 0.73 V (ΔE_{ρ} = 74 mV) in **7** and $E_{1/2}^{1} = -0.32 \text{ V} (\Delta E_{p} = 57 \text{ mV})$ and $E_{1/2}^{2} = -0.71 \text{ V} (\Delta E_{p} =$ 65 mV) in 8. Gratifyingly, as compared to their dibromo counterpart 4 and 5, the $E_{1/2}^1$ and $E_{1/2}^2$ potential values were cathodically shifted by ca. 115 mV and ca. 190 mV, respectively.

Apart from that, modulation effect was also investigated on the wave separation (ΔE) between both the redox signals ($E^{t}_{1/2}$ and $E^{2}_{1/2}$). For example, in dibromo NDIs **3**, **4** and **5**, ΔE values were observed to be 490 mV, 460 mV and 470 mV, respectively.



Figure 3. Cyclic voltammogram of 1, 2, 4–9 in DCM and 3 in DMF 0.1 M $Bu_4 \text{NPF}_6,$ potential is referenced against standard calomel electrode (SCE). $^{[31]}$

Whereas, this separation is reduced to 360 mV for sulphur substituted NDI (6). On the other hand, traversing from dibromo NDIs 4 and 5 to their respective tetrabromo counterparts 7 and 8 respectively, exhibit comparatively compressed $E^{1}_{1/2}$ and $E^{2}_{1/2}$ separation of 350 mV (7) and 380 mV (8). These results further established the large electronic impact on modification in the NDI-core. Furthermore, the octabrominated perylenediimide (9)^[3b] showed further shifts in redox potentials towards the positive side of voltammogram with $E^{1}_{1/2}$ at -0.17 V (ΔE_{p} = 97 mV) and $E^{2}_{1/2}$ at -0.34 V (ΔE_{p} = 105 mV). These results suggest that increase in the number of π -*rings* as well as the core-substitution of bromine atom(s) affords more electron deficient scaffolds, which in turn facilitates the electron accepting properties of the imides.

Table 2. Cyclic voltammetry studies of 1 – 9.							
Molecule	E ¹ _{1/2} (V)	E ² 1/2 (V)	ΔE	LUMO (eV) ^a			
1	-1.09			-3.304			
2	-0.68			-3.491			
3	-0.47	-0.90	0.49	-3.989			
4	-0.49	-0.95	0.46	-3.874			
5	-0.44	-0.91	0.47	-4.018			
6	-0.20	-0.56	0.36	-4.197			
7	-0.38	-0.73	0.35	-3.962			
8	-0.32	-0.71	0.38	-4.076			
9	-0.17	-0.34	0.17	-4.229			

Condition: 1, 2, 4–9 in DCM and 3 in DMF 0.1 M Bu₄NPF₆; ^aCalculated for reduction potential: -(4.4+ $E^{\rm 1}_{\rm red}).$

Single crystal X-ray Crystallography Studies

Gratifyingly, we could obtain good quality single crystals of all the compounds and investigate their propensity to form halogen bonding interactions by X-ray diffraction studies. Figure 4 shows the molecular structures of compounds 1-8.^[21,32]

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Figure 4. Single crystal X-ray structures of molecules 1-8. Thermal ellipsoids are drawn at 50% probability level.

Interestingly, all the compounds showed multiple Br···Br and/or Br···O_{imide} halogen bonding interactions (Table S1). Modulation in the size of the imide rings (five Vs six) and the π -scaffold reflected considerable influence on the intramolecular Br···O_{imide} separation.



Figure 5. A side view of the single crystal X-ray structure of molecule **9**. Thermal ellipsoids are drawn at 50% probability level.

Notably, crystal structure of 1 displays intramolecular Br ... O separation of avg. 3.175 Å (Br1···O1 = 3.173 Å and Br4···O2 = 3.178 Å) which increases to 3.199 Å (Br1'...O1) and 3.238 Å (Br1...O2) in 2. However, in the NDI-based compounds 3-8 a considerable decrease in the intramolecular Br...O separation in the range 2.861–2.937 Å was observed. Tetrabromination at the core in 7 and 8 influence the intramolecular Br...O separation as well as the planarity of the NDI scaffold. For example, 7 shows Br···O separations of 2.861 Å (Br2···O2) and 3.025 (Br1···O1) Å, while 8 exhibits Br···O separation of 2.919 Å (Br2···O2) and 2.937 Å (Br1…O1). Likewise, Br…O interactions in 9 was found to be 2.831 and 2.870 Å (Figure 5). It is important to note that the intramolecular Br...O interactions revealed in 1-9 are considerably shorter than the sum of the van der Waals radii of Br and O atoms (3.45 Å).^[22] Structural analysis of **7** and **8** reveals highly twisted NDI scaffolds with torsional angle (θ) of 16.65° (O1-C5-C1-C7) and 7.23° (O2-C4-C3-C6) in 7 and 23.44° (O2-C6-C4-C3) and 19.90° (O1-C7-C1-C2) in 8. The increased torsion angle in 8 is possibly influenced by the bulky mesityl rings. Notably, such twisted non-planar arrangement of the aromatic core was also observed in case of octa-brominated PDI 9.[3b]

Table 3. Halogen bonding interactions and torsion angle in 1 - 9.								
Mo lec ule	Intramolecular	separation	Intermolecula	Torsion				
	Br…O _{imide}	Br…Br	Br…O _{imide}	Br…Br	angle ^a			
1	3.173(5), 3.178(4)	3.316(1) 3.275(1) 3.306(1)	3.051(6)	3.695(9) 3.686(1) 3.670 3.713	2.68			
2	3.199(2) 3.238(2)		2.981(2)	3.707(4)	4.45			
3	2.888(4)	3	3.244(3)	3.705(8)	0.32			
4	2.912(2)				5.76			
5	2.935(2)		3.513(2)	-	2.28			
6	2.907(2)		3.175(2)	3.602(3)	0.14			
7	3.025(1) 2.861(1)	3.197(1)	3.081(8)	3.433(1), 3.633(1)	12.90, 3.25			
8	2.937(6), 2.919(5)	3.174(1)	3.101(5),		5.69, 2.11			
9	2.831 2.870	3.210 3.238 3.357	3.255(4) 2.794(3)					

^a(O-C1-C2-C3-Br), (Br-C2-C4-Br)

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Further, all the compounds exhibit extensive intermolecular halogen bonding interactions resulting in the formation of self-assembled structures (Figures S18-S25; ESI). Moreover, depending upon the angle formed between the two C–X···Y–C (X = Br and Y = Br/O) synthons (Figure 6), these interactions are classified as type I (symmetrical interactions where $\theta_1 \approx \theta_2$) and type II (bent interactions where $\theta_1 \approx 180^\circ$ and $\theta_2 \approx 90^\circ$).^[23,24]

In case of **1**, two molecules in one-dimension (1D) layer (shown in same colour) interacts via intermolecular Br···O_{imide} separation of 3.052 Å (Br1···O1) and Br···Br separation of 3.696 Å (Br1···Br1') and 3.686 Å (Br1···Br2') (Figure 7a). In Br···O interaction, \angle C3--Br1···O1 (θ_1) and \angle C1--O1···Br (θ_2) were found to be ~ 177° and 158° respectively, suggesting type I interaction (Figure 6). Whereas, for the Br···Br interaction, a non-ideal type II like interaction was observed with the θ_1 (\angle C3--Br1···Br2) and θ_2 (\angle C4--Br2···Br1) of ~ 177° and ~ 122°, respectively. As a reference, the sum of the van der Waals radii of two Br atoms has been found to be 3.74 Å.^[22]



Figure 6. Type I and type II interactions in halogen bonded systems.

Moreover, the 1D arrangement in 2 involves type I intermolecular Br...Br and Br...O interactions having separation of 3.707 Å $(\angle C2'$ —Br1'···Br1—C2; $\theta_1 = \theta_2 = 121.49^\circ$) and 2.981 Å (C2'— Br1'···O2—C5; $\theta_1 = \sim 177^\circ$, $\theta_2 = \sim 158^\circ$), respectively (Figure 7b). Interestingly, type I interactions in 3 displays 1D arrangement having Br...Br (3.707 Å) separation identical to 2, but the Br...O separation increased to 3.256 Å (C2'-Br1'···O2-C7) due to the possible increase in size of the π -scaffold (Figure 7c). In contrast, presence of alkyl and bulky mesityl groups in the axial positions of 4 and 5 respectively, shows layered structure involving only weak Br...O and no Br...Br intermolecular interaction with the separation of 3.736 Å in 4 and 3.513 Å in 5 (Figures 7d-e). Importantly, both 4 and 5, demonstrate type II interaction with θ_1 $(\angle C2$ —Br1···O2) = ~86° and θ_2 ($\angle C6$ —O2···Br1) = ~141° in **4** and $\theta_1 (\angle C3$ —Br1···O2) = ~87° and $\theta_2 (\angle C7$ —O2···Br1) = ~137° in **5**. Interestingly, **5** shows $Br \cdot \cdot \pi$ interactions with distances ranging between 3.190-3.389 Å. However, 6 demonstrates Br...Br and Br...O intermolecular interaction of type I separated by 3.602 Å and 3.175 Å respectively, resulting in the generation of 1D layer (Figure 8a). Moreover, structural complexity in 7 gets reflected in its intermolecular interaction where one molecule is connected to symmetrically arranged four adjacent neighbors in a zig-zag manner via four Br···O (Br2'···O1A: 3.081Å) and eight Br···Br (Br1…Br2': 3.633 Å and Br2…Br1': 3.433 Å) interactions (Figure 8b). Interestingly, while Br...O interaction followed type I mode of interaction, Br...Br shows type II interaction.



Figure 7. Representation of Br···O, Br···Br and Br··· π halogen bonding interactions in molecules **1-5** and their self-assembly. Color code: H, White; C, Gray; N, Blue; O, red and Br, orange.

While **8** having bulky mesityl groups in the axial positions, interact symmetrically with four neighboring molecules only through Br···O (Br1···O2': 3.101 Å) forming type I interactions with no observable Br···Br interactions akin to that of **5** (Figure 8c). Finally, in **9** only

the Br atoms at the bay positions participate in halogen bonding Br···O type I interactions with θ_1 and θ_2 being ~163° and ~174° (Figure 8d).

Consequently, the question is how does these halogen bonding interactions influence or drive the hierarchical selfassembly? Considering the self-assembly of 1, the Br...Br interactions form 5-, 9- and 12-membered large-sized rings to propagate the two distinct 1D layers, as highlighted with different color codes (Figure 7a, Table S2). The 5-membered rings are shaped via three Br atoms with distances of 3.686 and 3.696 Å, amongst which one of the Br atoms forms a bifurcated, or a threecenter halogen bonding interaction. Interestingly, the 12membered rings which are formed through the participation of six Br atoms have two 9-membered rings inscribed in it. The 9membered rings are formed through halogen bonding interactions between five Br atoms. In contrast, a smaller 6-membered ring is formed by the participation of one O atom and two Br atoms, with Br1' forming a bifurcated halogen bonding interaction. As a result, two distinct 1D lavers are formed, which are connected via Br...Br (Br2...Br2': 3.713 Å and 3.670 Å) interactions resulting in the formation of 1D sheets (Figure S18a; ESI). Interestingly, these 1D sheets form infinite m-stacks via interlayer H-bonding between alkyl hydrogen (H10) and Oimide (O1) atoms (Figure S18b; ESI). In case of 2, a large 10-membered ring is formed via the formation of two short Br...O (2.981 Å) interactions. This large ring has two 6-membered rings inscribed in it that is linked via a Br...Br interaction (3.707 Å). These halogen bonded rings continue to form infinite 1D layers, which are connected via interlayer Hbonds between hydrogen atoms (H9a and H9b) of the axial alkyl chains and Oimide (O1) of another layer (Figure S19; ESI). Likewise, 3 forms similar supramolecular halogen bonded rings, which replicate to form infinite 1D layers. Further, these layers form π - π stacking interactions to afford 2D sheets (Figures S20; ESI). In contrast, 4 forms a 1D layer aided by 10-membered rings carved out of two complementary C-H···O H-bonding interactions, while extremely weak Br...O interactions were observed. These 1D layers further π -stack via the naphthyl rings to afford 2D sheets (Figure S21; ESI). Such preference of H-bonding has been seen in pyridine-N-oxide versus halogen bonding in pyridine-based scaffolds substituted with halogen atoms.^[25] In case of 5, the 1D layer is formed by a combination of C-H-O H-bonded 10membered rings, weak 5-membered Br---O rings and multiple Br \cdots π halogen bonding interactions. Thus, the bulky axial mesityl groups in 5 entails complexity in the infinite supramolecular organization (Figure S22; ESI). In 6, the halogen bonded rings are formed in a similar fashion to that of 3, while surprisingly the mesityl rings do not induce any Br $\cdots \pi$ interactions. Moreover, Hbonding interactions involving hydrogen atom (H10) of the axial mesityl group with the O_{imide} (O1) of another layer assist formation of 2D sheets (Figures S23c; ESI). In the case of 7, multiple Br...O, Br...Br and Br... π interactions result in the propagation of the supramolecular assembly. In particular, highly unusual trifurcate type of halogen bonding interactions, in which a Br atom forms two Br…Br and one Br…O type of interaction, while the adjacent Br atom can form another trifurcate type of halogen bonding interactions with two Br…Br and one Br… π interactions. Interestingly, the NDI ring participates to form the Br $\cdot\cdot\cdot\pi$

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interaction. The supramolecular packing of **7** shows the presence of 2D arrangement comprising



Figure 8. Representation of Br···O, Br···Br and Br··· π halogen bonding interactions in molecules **6-9** and their self-assembly. In case of **9**, the central PDI molecule is colored Pink to aid in deciphering the interactions. Color code: H, White; C, Gray; N, Blue; O, red and Br, orange.

of vertically propagating two different layers (shown in green and blue colour) (Figure S24b; ESI). In sharp contrast, 8 forms a supramolecular assembly in which the essential halogen bonding interactions are very different to that of its congener 7. Molecule 8 assembles involvement of four Br...O interactions and an equal number of Br $\cdot\cdot\cdot\pi$ interactions in a radial manner. This results in a 2D sheet type of an arrangement (Figure S25a; ESI). Interestingly, the well-aligned 2D sheets are placed over one another via π stacking of xylene solvent molecules (with distance of ca. 3.473 Å and 3.541 Å) (Figures S25b and c; ESI). Noteworthy here is, that the asymmetric supramolecular packing in 8 produces a noncentrosymmetric Fdd2 space group, while all the other molecules considered here crystallizes in a centrosymmetric manner (Table S5-6). Notably, 9 having the largest π -surface amongst all the considered molecules, shows multiple Br···O and Br··· π halogen bonding interactions. The Br atoms at the non-bay positions (Br1, Br4) form Br $\cdots\pi$ halogen bonding interactions with the PDI rings of the neighboring molecules with Br1...C12 and Br4...C3 distances being 3.516 and 3.347 Å, respectively. The Br atoms at the bay positions (Br2, Br3) form Br...O halogen bonding interactions with Br2···O2 and Br3···O1 distances being 2.794 and 3.255 Å, respectively. The increased number of Br $\cdot\cdot\cdot\pi$ halogen bonding interactions is possibly due to the ring contortion brought about by the perbromination as also observed in the case of 7. The contortion drives large overlapping of the π -surfaces and the consequent 2D corrugated sheet-like self-assembly. The Br $\cdot\cdot\cdot\pi$ interactions observed in case of 5, 7, 8 and 9 can be termed as multi-center halogen bonding as the Br atom forms multiple sub van der Waals interactions (3.64 Å).

Hirshfeld surface analysis

Hirshfeld crystal surface analysis and fingerprint plots facilitates a comparison of the inter and intra-molecular non-covalent interactions such as Br····O, Br···Br, π ··· π , O···H interactions within the molecules.^[26,27] In order to gain insight into these interactions, Hirshfeld analysis for all the synthesised molecules were performed (Figure S26-S35). As shown in table 4, molecule 1 exhibit highest value for intermolecular Br····Br interaction of 26.4% whereas 7 displays maximum Br···O interaction of 10.0%. Importantly, surface analysis clearly showed absence of Br···Br interactions in 4 and 5, while sparser Br···O interaction. In general, traversing from 1-9, the Br···O interaction is significantly more common (except that for 1) than Br···Br interaction. Hirshfeld analysis also captured significant amount of Br···C interactions in the crystal structure, out of which, significant proportion arise from well-defined Br··· π interactions.

Topological Analysis

Next, we performed computational topological analysis for all the halogen bonded systems.^[28,29] Topological calculation of the electron density supports the presence of potential halogen bonds in all the compounds. Importantly, the bond critical points (BCP) were observed existing in a bond path of two interacting atoms (e.g. Br \cdots O and Br \cdots Br). Table 4 and S3 describe the calculated local properties at Br \cdots O and Br \cdots Br BCPs in all the halogenated

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systems. Primarily, these properties at the BCPs are analysed based on the different parameters: the electron density $\rho(\mathbf{r}_{c})$ and Laplacian $\nabla^2 \rho(\mathbf{r}_c)$, the densities of kinetic energy, $G(\mathbf{r}_c)$, potential energy, $V(\mathbf{r}_c)$, total energy, $H(\mathbf{r}_c) = V(\mathbf{r}_c) + G(\mathbf{r}_c)$, and the $|V(\mathbf{r}_{c})|/G(\mathbf{r}_{c})$ ratio. Notably, the Laplacian of the electron density is related to the measure of the local curvature of $\rho(r_c)$, and illustrates whether the electron density is locally depleted ($\nabla^2(\mathbf{r}_c)$) > 0) or concentrated ($\nabla^2(\mathbf{r}_c) < 0$) at any given point in the space. Furthermore, the Laplacian is related to the local potential ($V(r_c)$) and kinetic $(G(\mathbf{r}_{c}))$ energy components of the total energy via virial theorem $(1/4)\nabla^2 \rho(\mathbf{r}_c) = 2G(\mathbf{r}_c) + V(\mathbf{r}_c)$ (in a.u.). Thus, when the $\nabla^2 \rho(\mathbf{r}_c)$ is negative, the electronic charge is concentrated and thus potential energy largely dominates the local total electronic energy $E(\mathbf{r}_{c})$ as well as the local virial relationship. Moreover, when the $\nabla^2 \rho(\mathbf{r}_c)$ is positive, the electronic charge is locally depleted and the kinetic energy is in local excess. According to Bader and Essen, the former condition occurs in shared interactions, while the later situation is the characteristic of closedshell interactions.[28]

AIM studies were performed by considering all the molecules in their dimeric form. The parameters obtained from the calculation are shown in table 4 and figures 9, S36 and S37. For intermolecular interaction, the values of $\rho(r_c)$ are calculated to be in a range of 0.0038-0.0217 au, whereas the values of $\nabla^2 \rho(r_c)$ are all positive, ranging from 0.0134 to 0.0758 au. These values are within the common accepted values for H-bonding interactions [28] and indicate closed-shell interactions in these molecules. In order to gain insight of non-covalent interaction, it is more appropriate to understand in terms of electron energy density $E(r_c)$. The sign of $E(r_c)$ at BCP indicates whether the interaction is electrostatic $(E(r_c) > 0)$ or covalent dominant $(E(r_c) < 0)$. From table S3, it is evident that for all the dimeric system in molecules 1 to 9, the $E(r_c)$ values are all greater than zero, which suggests that the halogen bonding interaction in these molecules are potentially electrostatic in nature. Notably, the intermolecular Br...O interaction (cp1) of molecule 4 (0.0007) and 9 (0.0023) exhibit minimum and maximum $E(r_c)$ values, respectively. Moreover, molecules 1 (0.0092), 2 (0.0107), 7 (0.0108) and 9 (0.0161) with axial alkyl chain, displays considerably increased electron density ($\rho(\mathbf{r}_{c})$) in

the intermolecular Br...O interaction as compared to other molecules. These observations were also noted in the laplacian electron density $\nabla^2(r_c)$ for the intermolecular Br...O interaction at the same BCP with molecule **9** exhibiting highest $\nabla^2(r_c)$ value of 0.0677 a.u. This value suggests strongest halogen bonding interaction which is also demonstrated by the shortest intermolecular Br···O distance of 2.831 Å in 9. In addition, the $\rho(r_c)$ values of the Br...O interaction can be seen to be dependent on the electron deficiency of the molecule. For example, 6 which is the second-most electron deficient molecule in the series (from CV studies), shows a $\rho(\mathbf{r}_{c})$ value of 0.0073 compared to 0.0038 and 0.0056 for 4, and 5, respectively. On the other hand, AIM results predict the absence of Br...Br intermolecular interaction in 4, 5 and 8 which is in further support of our crystallographic findings. Interestingly, in 7, significantly high Br...Br interactions with electron density 0.0048, 0.0080 and 0.0099 a.u. at cp2, cp3 and cp4 respectively, were observed. Figure 9, S36 and S37 displays molecular critical points and contour maps of all the nine molecules. Thus, topological analysis at the BCPs validates intermolecular Br...Oimide as well as Br...Br interactions in these systems.

Natural Bond Orbital analysis

NBO analyses provide an efficient tool in understanding intra and intermolecular bonding and interaction among bonds, as well as provides a convenient ground for investigating conjugative interactions or charge transfer in molecular systems.^[30] Moreover, NBO method provides advantage in getting information about interactions in both filled and virtual orbital spaces that could influence the intra and intermolecular interactions analysis. Herein, we have identified two representative molecules **1** and **3** based on their small size and structural diversity to perform NBO analysis. The second order Fock matrix aids to evaluate the donor-acceptor orbital interactions.^[30,31]

	cp1				ρ(r _c) ^a				Hirshfeld surface (%)		
		cp2	ср3	cp4	cp5		Br⋯O	Br⋯Br	Br⋯O	Br⋯Br	Br⋯C
1 0.	0.0092	0.0113	0.0112	0.0069	0.0058	0.80	1.61	1.57	4.7	26.4	19.4
2 0.	0.0107	0.0067	0.0101	0.0107		1.90			7.2	1.5	13.9
3 0.	0.0059	0.0064	0.0189	V		1.71	1.29	0.50	5.1	2.5	0.0
4 0.	0.0038	0.0085	0.0038	0.0183		1.13	-		0.0		5.2
5 0.	0.0056	0.0092	0.0092	0.0056	0.0176		-		0.8		4.2
6 0.	0.0073	0.0081	0.0073	0.0185	0.0185		-		3.4	1.0	
7 0.	0.0108	0.0048	0.0080	0.0099	0.0147		-		10.0	6.4	14.9
8 0.	0.0089	0.0183	0.0177	0.0195			-		5.3	0.8	4.9
9 0.	0.0161	0.0063	0.0217	0.0080			-		8.6	6.2	17.5

Table 4: Intra and Intermolecular cp (critical point) values, Potential energy difference, Second order perturbation energy, Hirshfeld interactions.

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Figure 9. Molecular critical point and contour line diagrams for the dimeric form of 1-4 molecules.

The E^2 value represents the extent of interaction between electron donors and acceptors. As shown in figure 10, two adjacent molecules of **1** exhibits interaction of non-bonding orbital of imide O lone-pair to antibonding Br-C orbital ($n_{Olp} \rightarrow \sigma^*_{Br-C}$) and the nonbonding Br lone-pair to antibonding Br-C orbital ($n_{Brlp} \rightarrow \sigma^*_{Br-C}$) with second order perturbation energy, E^2 of around *ca.* 1.61 kcal/mol and 1.57 kcal/mol, respectively. The 3D (Figure 10 a,c) and 2D (Figure 10 b,d) representations clearly showed non-bonding and antibonding orbital overlaps.





Figure 11. NBO 2D and 3D representation of intermolecular donor–acceptor O···Br and Br···Br interactions in **3**. (a, b) Overlap between *n* and σ^* orbitals in O···Br. (c and d) Insufficient overlapping between *n* and σ^* orbitals in Br···Br.

Whereas, the dimeric form of **3**, exhibits $n_{\text{Olp}} \rightarrow \sigma^*_{\text{Br-C}}$ interaction within the ten-membered cyclic ring with E^2 of 1.29 kcal/mol (Figure 11 a-b) and $n \text{Br}_{\text{Ip}} \rightarrow \sigma^*_{\text{Br-C}}$ interaction with greatly reduced E^2 value of 0.50 kcal/mol (Figure 11 c-d). The calculations revealed greater stabilization from the Br...O interactions vis-à-vis the Br...Br interactions. The NBO calculations also clearly established the donor-acceptor type of interactions between the non-bonding lone-pair orbitals of O/Br and the antibonding orbitals of Br-C.

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A Predictive Design Tool-Box?

With the information in hand, is it possible to arrive at a general tool-box that can aid or help to forecast the various probable halogen bonding interactions in the solid-state for arylene-imide/-diimide-based systems? Towards this, we consider here a simple flow-chart that starts with the various available input variables in the molecular structure (Figure 12).



Figure 12. A flow-chart for halogen bonding (XB) in arylene-imides and - diimides to accomplish a predictive structural design tool-box.

The system can then form halogen bonding of different types including complex possibility of a combinational halogen bonding that utilizes all the three types e.g., Br···O, Br···Br and Br··· π interactions. The interactions can then form hierarchical assembly depending on the halogen bonded ring-size, no. of different halogen bonded rings, a simple two-center versus three-center (bifurcated) or multi-center interactions. These interactions can lead to the self-assembled D/2D sheets or non-planar corrugated sheets. At this point, we can consider the possible outlier(s), which provide orthogonal insight into the halogen bonding interactions. For example, a molecular system (*vide*, example 4) that prefers to form C–H···O H-bonding interaction over halogen bonding interaction. There can be other outliers that result from asymmetric hierarchical assembly of the molecules to result in

non-centrosymmetric packing (*vide*, example **8**). In the next level, predictive computational tools aid in determining and validating the $\rho(r)/E^{(2)}$ parameters of the halogen bonding interactions. A systematic logical understanding can thus assist to establish a predictive structural tool-box in these systems.

Conclusions

In summary, we explored the halogen bonding properties of di-, tetra- and octa-brominated arylene-imide/-diimide-based electron deficient π -scaffolds of varying sizes, e.g. from the small PTMI, to the moderately-sized PMDI and NDIs, to the large PDI. In a set of nine molecules, we also varied the axial-groups, number of halogens, and imide carbonyl O versus S atoms to examine how these diverse modifications influence the halogen bonding and its self-assembly. The molecules showed tunable optical and redox properties and also demonstrated deep-lying LUMOs with values reaching -4.2 eV. Importantly, we realized single crystals of all the nine systems and X-ray diffraction studies revealed three-types of halogen bonding interactions viz. Br...O, Br...Br or Br... π . Notably, few of the systems could exhibit a combination of all the threetype of interactions. In general, the Br…O interactions outnumber the Br…Br interactions. The Br… π interactions evolve as a result of the mesityl groups at the axial positions, or as a result of the contortion in the arylenediimide rings. Interestingly, we observed 5-, 6-, 9-, 10- and 12-membered diverse halogen bonded rings. The mono-, bifurcated- or multi-center halogen bonds further propagate to form stacked 1D-, 2D- or corrugated sheets. The study also recognized few outliers, e.g. molecule which prefer C-H···O hydrogen bonding over halogen bonding interactions; or a non-centrosymmetric organization over the majority of centrosymmetric ones. Such non-centrosymmetric arrangement would be of great interest from the point of view of designing new class of supramolecular NLO systems.[32] Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) analysis provided insight into the halogen bonding interactions. The $\rho(\mathbf{r}_{c})$ values also reflected the effect of the electron deficiency of the molecule on the halogen bonding interactions. The findings outlined here, can be considered as a predictive design tool-box for higher-order arylenediimides and for other related halogen bonded electron deficient π -systems.

Experimental Section

General: All starting materials and reagents were purchased from commercial sources and used without further purification, unless otherwise stated. NMR spectra were recorded on a Bruker 500 MHz spectrometer. ¹H, ¹³C, DEPT-135 and APT NMR spectra were recorded using TMS as an internal standard. Spectra were referenced to residual solvent peaks. Chemical shifts (δ) were expressed in ppm. Coupling patterns were designated as s, singlet; d, doublet; t, triplet; m, multiplet. TOF-MS-ES mass spectral data were obtained using a Synapt G2 HDMS mass recorded spectrometer. UV-Vis-NIR spectra were on a JASCO V-670 Spectrophotometer; path lengths of 10 mm were used. Wavelengths reported in nanometers (nm). UV-Grade solvents were used for the spectroscopic experiments. FTIR spectra were recorded on a Varian 7000 FTIR spectrometer. Samples were prepared in a dry condition. A background scan of air was collected prior to analysis while FTIR in neat were taken using Bruker Tensor 37 FTIR Spectrometer.

Electrochemical measurements: Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement consisted of platinum as a working and auxiliary electrodes and SCE as reference electrode. All the electrochemical measurements were carried out in Ar-purged solvents containing nBu_4NPF_6 (0.1 M) as the supporting electrolyte. The scan rate for CV experiments was typically 200-300 mV/s. DPV was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.^[33]

X-ray Crystallography: The intensity data were obtained with Bruker APEX-II CMOS diffractometer for 1-8 by using graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz polarization effects and an empirical absorption correction (SADABS) was applied. The structures were solved by direct methods and refined by fullmatrix least-squares refinement techniques on F^2 by using the programs SHELXL-2016 in the WinGX module.[34] All hydrogen atoms were fixed at calculated positions with isotropic thermal parameters, whereas all nonhydrogen atoms were refined anisotropically. In 7, four carbon atoms (C8, C9, C10, C11) of butyl alkyl chain and two imidic oxygen atoms O1 and O2 were found disordered and were fixed at two positions using part command. In addition, one nitrogen (N1) and a carbon atom (C5) were refined isotropically. Moreover, in 3, 6 and 7, some disordered electron density was observed which could not be resolved. In case of 3 and 6, disordered electron density was removed using solvent masking procedure 'SQUEZE' in PLATON showing the electron recovery of 72 in 3 and 46 in 6. These electron counts closely corresponds to one dimethylacetamide and dichloromethane solvent molecule in 3 and 6. respectively. Whereas in case of 7, squeezing the electron density lead to unstable structural refinement, and therefore are not squeezed due to which the CHECK CIF displays B-level alert of residual electron density. However, in case squeezed, the squeeze command leads to the recovery of electron count of 89 corresponding to a toluene molecule. All the crystallographic details and refinement parameters are provided in tables S4 and S5; ESI. CCDC 1869948-1869955 contains supporting crystallographic data for this paper.

Synthesis

Synthesis for 3,6-Dibromopyromellitic acid precursor for the **1** and **2** as well as Br₂NTCDA and Br₄NTCDA was performed according to the literature report.⁽²⁰⁾ Whereas, **9** was synthesised as reported earlier by our group.^(3b)

Synthesis of 1: A mixture of tetrabromophthalic anhydride (1.00 gm, 2.10 mmol) and butyl amine (8.60 mmol) in acetic acid (25.0 ml) was stirred at 80°C for 3h. The reaction mixture was cooled and filtered to afford dirty white precipitates. These precipitates were thoroughly washed with methanol and then acetone (one time) and air dried under vacuum to obtain off-white crystalline solid. Yield: 380 mg (30 %), R_f = 0.57 (CHCl₃/Hexane 8:2), M.P.>300 °C, ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 3.63 (t, 2H, J = 7.0 Hz), 1.61-1.53 (m, 2H), 1.32-1.25 (m, 2H), 0.87 (t, 3H, J = 7.0 Hz). ¹³C NMR (125 MHz, CDCl₃, 300 K): δ = 163.88, 143.30, 137.43, 130.88, 130.67, 130.50, 128.96, 128.79, 128.39, 125.42, 121.21, 63.22, 38.87, 30.39, 30.25, 20.05, 13.59. FTIR (neat, cm-1): 2936, 2853, 1688, 1331, 1156. ESI-MS: calculated exact mass for [C₁₂H₁₀Br₄NO₂ + H^{*}], 515.7440, found 515.3732.

Synthesis of 2: A mixture of 3,6-dibromopyromellitic acid (1.00 gm, 2.60 mmol) butyl amine (10.60 mmol) and acetic acid (25.0 ml) was stirred at 80°C for 3h. The mixture was cooled to room temperature, the precipitated was collected by filtration and washed with three times methanol and once with acetone and dried under vacuum to obtain off-white crystalline solid. Yield: 391 mg (33 %), Rf = 0.72 (CHCl₃/Hexane 8:2), M.P.>300 °C, ¹HNMR (500 MHz, CDCl₃, 298 K): δ = 3.67 (t, 4H, J = 7.0 Hz), 1.64-1.55 (m, 4H), 1.34-1.27 (m, 4H), 0.90 (t, 6H). ¹³C NMR (125 MHz, CDCl₃, 300 K): δ =

163.50, 136.18, 114.07, 38.86, 30.25, 20.06, 13.58. FTIR (neat, cm-1): 2919, 2853, 1771, 1705, 1439, 1364, 1181. ESI-MS: calculated exact mass for $[C_{18}H_{20}Br_2N_2O_4+2H^*],$ 485.9779, found 485.8675.

Synthesis of 3: A mixture of Br₂NTCDA (1.00 gm, 2.34 mmol) and ammonium acetate (2.80 g, 37.52 mmol) in acetic acid (25.0 ml) was stirred at 80 °C for 6 h. The reaction mixture was cooled to room temperature to afford yellow precipitates. These precipitates were filtered and washed with methanol (three times) followed by acetone (one time) and was air dried under vacuum to obtain yellow product. Yield: 397 mg (40%). M.P.>300 °C, ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ (ppm) = 12.28 (d, 2H, *ArH*-axial), 8.63 (d, 2H, *ArH*). FTIR (neat, cm-1): 3202, 3078, 2869, 1671, 1563, 1414, 1247. ESI-MS: calculated exact mass for [C₁₄H₄Br₂N₂O₄ + 2H⁺], 423.8683, found 423.5392.

Synthesis 4: A reaction procedure similar to **3** was performed in acetic acid with the following reagents; Br₂NTCDA (1.00 gm, 2.34 mmol) and hexylamine (1.22 ml, 9.36 mmol). Reaction mixture was stirred for 90 min followed by regular workup with methanol and acetone to afford yellow colour product. Yield: 485 mg (35 %), R_f = 0.72 (CHCl₃/Hexane 7:3), M.P.>300 °C, ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 9.02 (s, 2H, *Ar-H*), 4.22 (d, 4H, *Ar-H*), 1.763-1.049 (16H), 0.93 (2x*CH*₃). ¹³C NMR (125 MHz, CDCl₃, 300 K): δ = 160.77, 160.73, 139.07, 128.33, 127.75, 125.38, 124.12, 41.62, 31.46, 29.70, 27.86, 26.74, 22.54, 14.01. FTIR (neat, cm-1): 3052, 2919, 2845, 1705, 1647, 1555, 1430, 1372. ESI-MS: calculated exact mass for [C₂₆H₃₀Br₂N₂O₄ + 2H⁺], 592.0561, found 592.7904.

Synthesis of 5: Reaction procedure similar to **4** was utilized for the using following reagents: Br₂NTCDA (1.00 gm, 2.34 mmol) and mesitylamine (1.32 ml, 9.36 mmol). Yield: 710 g (46 %), R_f = 0.52 (CHCl₃), M.P.>300 °C, ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 9.04 (s, 2H, *Ar-H*), 7.01 (s, 4H, *MesBz-H*), 2.31(s, 6H, *Mes-pCH3*), 2.03(d, 12H, Mes-CH₃). ¹³C NMR (125 MHz, CDCl₃, 300 K): 161.20, 160.57, 160.26, 160.22, 139.58, 139.37, 139.17, 138.99, 134.90, 134.81, 132.22, 131.52, 131.26, 130.55, 130.25, 130.11, 129.88, 129.68, 129.43, 129.04, 128.62, 127.14, 126.58, 126.44, 126.25, 124.49, 21.22, 17.82, 17.77. FTIR (neat, cm-1): 2919, 1721, 1671, 1563, 1406, 1297, 1223. ESI-MS: calculated exact mass for [C₃₂H₂₆Br₂N₂O₄ + 2H⁺], 660.0248, found 660.9420.

Synthesis of 6: Suspension of N,N'-dimesityl-1,4,5,8-tetracarboxylic acid bisimide (0.50 g, 0.76 mmol) and Lawesson's reagent (LR) (2.00 gm, 3.03 mmol) in dry and degassed toluene (20.0 ml) was heated at 85 °C for 36 h under N₂ atmosphere. The resulting brown solution was allowed to attain room temperature and concentrated under vacuum to afford brown solid. This solid was purified by column chromatography (100-200 mesh) with CHCl₃/Hexane (2:1) as an eluent. Yield: 102 mg (20%), R_f = 0.56 (CHCl₃/Hexane 6:4), M.P.>300 °C, ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 9.34 (2H, *Ar-H*), 6.99 (4H, Mes*Bz-H*), 2.31 (6H, Mes-*pCH*₃), 1.99 (12H, Mes-*oCH*₃), 13C NMR (125 MHz, CDCl₃, 300 K): δ = 189.30, 158.08, 143.68, 139.15, 135.38, 134.06, 129.77, 128.33, 128.27, 127.17, 123.54, 21.29, 17.72, 17.67. FTIR (neat, cm⁻¹): 2911, 1688, 1414, 1331, 1214. MS (MALDI-TOF, matrix-α-cyano-4-hydroxycinnamic acid): 552.46 (m/z).

Synthesis of 7: A mixture of Br₄NTCDA (1.00 gm, 1.71 mmol) and butyl amine (0.35 ml, 3.61 mmol) were taken in DCM (25.0 ml) and was refluxed for 2h. To the resulting reaction mixture PBr₃ (0.34 ml, 3.61 mmol) was added followed by stirring for another 1h. The mixture was allowed to attain room temperature. The resulting reaction mixture was poured onto ice cold water to afford yellow precipitate. This precipitate was filtered and washed with methanol (three times) and finally with acetone (one time). The obtained solid was dried under vacuum to obtain yellow crystalline solid. Yield: 392 mg (33 %), R_f = 0.68 (CHCl₃/Hexane 8:2), M.P. 300 °C, ¹H NMR (500 MHz, CDCl₃, 298 K): δ = 4.14 (t, 4H, J = 7.5 Hz), 1.70-1.64 (m, 4H), 1.42-1.35 (m, 4H), 0.94 (t, 6H). ¹³C NMR (125 MHz, CDCl₃, 300 K): δ = 159.82, 138.90, 135.60, 128.12, 127.67, 126.67, 125.66, 42.70, 42.29, 41.86, 37.11, 36.98, 32.80, 31.94, 29.99, 29.90, 29.71, 29.38, 27.28, 27.10,

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22.71, 20.41, 20.35, 14.14, 13.79. FTIR (neat, cm $^{-1}):$ 2919, 2861, 1705, 1655, 1364, 1272, 1189, 1147. ESI-MS: calculated exact mass for $[C_{22}H_{22}Br_4N_2O_4+4H^*],$ 693.8291, found 693.7791.

Synthesis of 8: Synthetic procedure similar to **7** was adopted for the synthesis of **8** using following reagents: Br₄NTCDA (1.00 gm, 1.71 mmol) and mesitylamine (1.32 ml, 9.38 mmol). Yield: 630 mg (45 %), R_f = 0.66 (CHCl₃), M.P. 300 °C, 'H NMR (500 MHz, CDCl₃, 298 K): δ = 7.01 (s, 4H, *MesBz-H*), 2.29 (s, 6H, *Mes-pCH*₃), 2.04 (d, 12H, *Mes-oCH*₃). ¹³C NMR (125 MHz, CDCl₃, 300 K): 159.81, 159.59, 139.50, 139.34, 139.28, 136.00, 134.74, 130.85, 129.71, 127.28, 126.25, 21.19, 17.90, 17.81. FTIR (neat, cm⁻¹): 3252, 2919, 1721, 1671, 1380, 1223.

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Herein, we explored the halogen bonding properties of aryleneimide/-diimide-based electron deficient scaffolds. We probed the influence of: scaffold size, axial-groups, number of halogens, and imide carbonyl O versus S atoms, on the halogen bonding and its self-assembly in a set of nine molecules. Single crystal X-ray data along with AIM and NBO analysis provide insight into these interactions.



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