#### **RESEARCH ARTICLE**



# Fluxional halogen bonds in linear complexes of tetrafluorodiiodobenzene with dinitrobenzene

Cai-Yue Gao | Bin-Bin Pei | Si-Dian Li 🗅

Institute of Molecular Science, Shanxi University, Taiyuan, China

#### Correspondence

Si-Dian Li, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China. Email: lisidian@sxu.edu.cn

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### Abstract

The fluxional nature of halogen bonds (XBs) in small molecular clusters, supramolecules, and molecular crystals has received considerable attention in recent years. In this work, based on extensive density-functional theory calculations and detailed electrostatic potential (ESP), natural bonding orbital (NBO), non-covalent interactions-reduced density gradient (NCI-RDG), and guantum theory of atoms in molecules (QTAIM) analyses, we unveil the existence of fluxional halogen bonds (FXBs) in a series of linear  $(IC_6F_4I)_m(OONC_6H_4NOO)_n$  (m + n = 2-5) complexes of tetrafluorodiiodobenzene with dinitrobenzene which appear to be similar to the previously reported fluxional hydrogen bonds (FHBs) in small water clusters  $(H_2O)_n$  (n = 2-6). The obtained  $GS \rightleftharpoons TS \rightleftharpoons GS'$  fluxional mechanisms involve one FXB in the systems which fluctuates reversibly between two linear C-I···O XBs in the ground states (GS and GS') via a bifurcated C-I<O<sub>2</sub>N van der Waals interaction in the transition state (TS). The cohesive energies ( $E_{coh}$ ) of these complexes with up to four XBs exhibit an almost perfect linear relationship with the numbers of XBs in the systems, with the average calculated halogen bond energy of  $E_{coh/XB} = 3.48 \text{ kcal} \cdot \text{mol}^{-1}$  in the ground states which appears to be about 55% of the average calculated hydrogen bond energy  $(E_{coh/HB} = 6.28 \text{ kcal} \cdot \text{mol}^{-1})$  in small water clusters.

#### KEYWORDS

first-principles theory, fluxional halogen bonds, fluxional hydrogen bonds, structural fluxionality, structures and bonding

# 1 | INTRODUCTION

Considerable attention has been paid to the study of non-covalent interactions<sup>1-3</sup> in crystal engineering,<sup>4,5</sup> supramolecular chemistry,<sup>6,7</sup> and biological medicines<sup>8-10</sup> in recent years. Hydrogen bonds (HBs) as the most frequently encountered non-covalent interaction have attracted great attention,<sup>11,12</sup> while halogen bonds (XBs) as another kind of typical non-covalent interaction also play a key role in both chemistry and materials science. A halogen bond Y—X…D is defined as the weak interaction between the halogen atom X as Lewis acid and electron donor D as Lewis base,<sup>13</sup> in which the halogen containing molecule Y—X is called the halogen bond donor and the Lewis base (D) the halogen bond acceptor, in analogy to hydrogen bonds.

The halogen atom X possesses a region of positive electrostatic potential (ESP) along the direction of Y—X bond called a  $\sigma$  hole,<sup>14–17</sup> while on the equatorial sides of X atom, a negative ESP is developed, so the X atom looks negative from equatorial directions and positive along the direction of Y—X bond.<sup>2</sup> Halogen bond belongs to a typical subset of  $\sigma$ -hole bonding.

Hassel et al. reported the first XB characterized by X-ray diffraction in 1954.<sup>18</sup> In the equilibrium structural unit of Br—Br···O (CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, the electropositive area of bromine atom on the Br—Br direction interacts with the more electronegative oxygen atom (O), forming a XB with the Br—Br···O angle close to  $180^{\circ}$ .<sup>19</sup> In 1985, Nyburg et al. confirmed that a C—Br···O XB is preferentially linear, with a C—Br···O bond angle close  $180^{\circ}$  and a Br···O distance smaller 2 WILEY- COMPUTATION

than the sum of the van der Waals radii of O and Br.<sup>20</sup> Many other studies also show that XBs tend to form linear structures<sup>21-25</sup> or monofurcated geometries.<sup>26</sup> Meanwhile, a halogen atom X can also form a bifurcated  $Y-X < D_2 XB$  interaction with two electron donors (D) coordinating one X atom, 27-29 similar to but different from the bifurcated HBs  $O \le H_2O$  observed in small water clusters.<sup>30</sup> Allen et al. experimentally synthesized the (IC<sub>6</sub>H<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) crystal (C2/m) of 1,4-diiodobenzene (IC<sub>6</sub>H<sub>4</sub>I) and 1,4-dinitrobenzene (OONC<sub>6</sub>H<sub>4</sub>NOO) in 1994 where the linear C-H-O HBs, linear C-H…I HBs, and bifurcated C-I < O<sub>2</sub>N non-covalent interactions coexist,<sup>31</sup> with HBs dominating the layered crystal structure of the system. Ji et al. theoretically predicted a series of complexes containing symmetrically bifurcated XBs which were late confirmed by the successful syntheses of their crystals.<sup>28</sup> Recently, Jain et al. synthesized a ternary crystal consisting of 4-nitrobenzaldehyde, tetrafluorodiiodobenzene and 1,4-diiodobenzene which also involve the symmetrical bifurcated C—I < O<sub>2</sub>N XB interactions.<sup>29</sup> However, if effective linear C—I…O XBs exist in small (IC<sub>6</sub>H<sub>4</sub>I)<sub>m</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO)<sub>n</sub> clusters or their derivatives, how linear C-I-O XBs and bifurcated C-I < O<sub>2</sub>N interactions fluctuate from one to another, and if there exists a phase transition in crystal (IC<sub>6</sub>H<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) under certain conditions still remain unknown both theoretically and experimentally.

Our group proposed the concept of fluxional bonds (FBs) in planar B<sub>19</sub><sup>-</sup>, tubular Ta@B<sub>20</sub><sup>-</sup>, and cage-like B<sub>39</sub><sup>-</sup> in 2019.<sup>32</sup> It is the multicenter covalent FBs that facilitate the structural fluctuation of these boron clusters. Similar intramolecular FBs were also found in other half-sandwich, planar or quasi-planar and tubular boron-based nanoclusters.<sup>33-41</sup> Typical  $\pi$ -FBs and  $\sigma$ -FBs also exist in the organic molecule bullvalene (C10H10) and its analogs.<sup>42,43</sup> In 2024, we unveiled the existence of fluxional hydrogen bonds (FHBs) in small water clusters  $(H_2O)_n$  (n = 2-6), extending the concept of intramolecular FBs to intermolecular non-covalent FHBs.<sup>30</sup>

Based on extensive non-covalent interaction analyses, we predict herein the existence of fluxional halogen bonds (FXBs) in  $(IC_6H_4I)$  $(OONC_6H_4NOO)$  and its linear derivatives  $(IC_6F_4I)_m(OONC_6H_4NOO)_n$ (m + n = 2-5) of tetrafluorodiiodobenzene (IC<sub>6</sub>F<sub>4</sub>I) with dinitrobenzene (OONC<sub>6</sub>H<sub>4</sub>NOO), extending the fluxional bonds from intramolecular FBs, intermolecular FHBs, to intermolecular FXBs. We found that, in the  $GS \rightleftharpoons TS \rightleftharpoons GS'$  fluxional processes, FXBs fluctuate reversibly from a linear C–I…O XB in the ground state GS through a bifurcated C-I<O2N van der Waals interaction in the transition state (TS) to a similar linear C–I…O XB in a neighboring GS', similar to the situations in the previously reported FHBs in small water clusters  $(H_2O)_n (n = 2-6).$ 

#### THEORETICAL METHODS 2

The GS and TS structures of  $(IC_6H_4I)(OONC_6H_4NOO)$  (1),  $(IC_6F_4I)$ (OONC<sub>6</sub>H<sub>4</sub>NOO) (2), (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (3), (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OON  $C_6H_4NOO_2$  (4), and  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$  (5) were optimized using the M06-2X method,<sup>44</sup> which has proven to be suitable for systems with XBs,  $^{45-47}$  with the 6-311 + G(d) basis sets used for C, H, O, N, and F<sup>48</sup> and Stuttgart/Dresden pseudopotential (SDD) employed for I, with the vibrational frequencies checked to ensure that all reported structures are true minima or transition states of the systems. As a comparison, structural optimizations are also performed on  $(IC_6F_4I)(OONC_6H_4NOO)$  (2) at  $\omega B97XD$ ,<sup>49</sup> PBE0,<sup>50</sup> and TPSSh<sup>51</sup> levels with the same basis sets, with the energy barrier further refined at the single-point CCSD(T) level<sup>52,53</sup> at the M06-2X geometries. The cohesive energies  $E_{coh}$  of the complexes were calculated according to Equation (1):

$$E_{\rm coh} = E_{\rm com} - {\rm Sum} \left( E_{\rm frag} \right) + {\rm BSSE}$$
 (1)

where  $E_{\rm com}$  is the total energy of the complex, Sum ( $E_{\rm frag}$ ) is the sum of the energies of the fragments, and BSSE represents the basis set superposition error corrections by the standard counterpoise method.<sup>54</sup> Intrinsic reaction coordinate (IRC) calculations were performed on the transition states TS (1), TS (2), TS (3), TS (4), and TS (5) to confirm the fluxional mechanism  $GS \rightleftharpoons TS \rightleftharpoons GS'$  of the concerned complexes.<sup>55,56</sup> All the calculations in this work were implemented using the Gaussian 16 package.<sup>57</sup> Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program.<sup>58</sup> To explore the nature of intermolecular non-covalent interactions, we carried out the ESPs, 59-61 non-covalent interactions-reduced density gradient (NCI-RDG).<sup>62</sup> and quantum theory of atoms in molecules (OTAIM) analyses<sup>63</sup> on the concerned systems using the Multiwfn program.<sup>64</sup> with the results visualized using the VMD software.<sup>65</sup>

#### **RESULTS AND DISCUSSIONS** 3

#### 3.1 Structures and stabilities

The optimized GS, TS, and GS' of  $(IC_6H_4I)(OONC_6H_4NOO)$  (1),  $(IC_6F_4I)$ (OONC<sub>6</sub>H<sub>4</sub>NOO) (2), (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (3), (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>  $H_4NOO_2$  (4), and  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$  (5) at M06-2X level are collectively depicted in Figure 1 which contain one, one, two, three, and four linear C-I-O XBs, respectively. Interestingly, as shown in Figure 1A, the bifurcated  $C_2$  (IC<sub>6</sub>H<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) (1) constructed from the experimentally observed crystal structure of  $(IC_6H_4I)$  $(OONC_6H_4NOO)^{31}$  corresponds to the transition state C<sub>2</sub> TS (1) with an imaginary vibrational frequency of 20.97i cm<sup>-1</sup>, while both the degenerate ground states  $C_s$  GS (1) and  $C_s$  GS' (1) contain a linear C-I---O XB without imaginary frequencies. Detailed IRC scanning indicated that the bifurcated  $C_2$  TS (1) can go back to  $C_s$  GS (1) or go forward to  $C_s$  GS' (1), forming a reversible GS (1)  $\rightleftharpoons$  TS (1)  $\rightleftharpoons$  GS' (1) fluxional mechanism with the two O atoms serving as electron donors and I atom as electron accepter. It has a halogen bond energy of 2.18 kcal·mol<sup>-1</sup> and activation energy of  $E_a = 0.24$  kcal·mol<sup>-1</sup>. As clearly demonstrated in Video S1, such a fluctuating processes with one FXB appears to be similar to the fluxional mechanism of water dimer  $(H_2O)_2$ .<sup>30</sup>

Substituting the four H atoms in fragment IC<sub>6</sub>H<sub>4</sub>I with four more electronegative F atoms, we obtain the complex  $(IC_6F_4I)$ 



Optimized structures of the ground states (GSs/GSs') and transition states (TSs) of (A)  $(IC_6H_4)(OONC_6H_4NOO)$  (1), (B)  $(IC_6F_4)$ FIGURE 1 (OONC<sub>6</sub>H<sub>4</sub>NOO) (2), (C) (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (3), (D) (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO)<sub>2</sub> (4), and (E) (IC<sub>6</sub>F<sub>4</sub>I)<sub>3</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO)<sub>2</sub> (5) at M06-2X level, with the optimized halogen bond lengths indicated in Å and the calculated cohesive energies  $E_{coh}$  and activation energy  $\Delta E_a$  indicated in kcal⋅mol<sup>-1</sup>.

(OONC<sub>6</sub>H<sub>4</sub>NOO) (2) of tetrafluorodiiodobenzene with dinitrobenzene in Figure 1B which also contains one linear C-I--O XB. As shown in Figure 1B and Video S2,  $(IC_6F_4I)(OONC_6H_4NOO)$  (2) possesses a similar  $C_s GS(\mathbf{2}) \rightleftharpoons C_{2v} TS(\mathbf{2}) \rightleftharpoons C_s GS'$  (2) fluxional mechanism with  $(IC_6H_4I)(OONC_6H_4NOO)$  (1), but the former has an obviously larger halogen bond energy of  $E_{\rm coh} = 3.66 \,\rm kcal \cdot mol^{-1}$  and a higher activation energy of  $E_a = 0.37 \text{ kcal} \cdot \text{mol}^{-1}$  than the latter. Substitution of four H atoms with four F atoms effectively enhances the  $\sigma$  hole on the I3 center and improve the strength of the XBs. As shown in Figure S1, the ωB97XD, PBEO, and TPSSh methods generate similar GS and TS structures and energy barriers with that of M06-2X, while the calculated CCSD(T) energy barrier of 0.42 kcal·mol<sup>-1</sup> well supports the corresponding value of 0.37 kcal·mol<sup>-1</sup> at M06-2X, evidencing the reliability of the theoretical approach used in this work.

The linear  $(IC_6F_4I)(OONC_6H_4NOO)$  (2) in Figure 1B can be extended readily to (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (3) in Figure 1C,  $(IC_6F_4I)_2(OONC_6H_4NOO)_2$  (4) in Figure 1D, and  $(IC_6F_4I)_3(OON)_2$ C<sub>6</sub>H<sub>4</sub>NOO)<sub>2</sub> (5) in Figure 1E with two, three, and four linear C–I…O XBs, respectively. Detailed IRC scanning processes clearly indicate that, in the GS  $\Rightarrow$  TS  $\Rightarrow$  GS' fluxional processes of these complexes (Figure 1C-E), there exists only one FXB which fluctuates reversibly from a linear C–I $\sim$ O XB in the GS via a bifurcated C–I<O<sub>2</sub>N in the TS to a linear C-I-O XB in GS'. The linear complexes (3), (4), and (5) with more than one XBs which exhibit similar fluxional mechanisms with that of  $(IC_6F_4I)(OONC_6H_4NOO)$  (2) possess the cohesive energies of  $E_{coh} = 7.14$ , 10.57, and 14.11 kcal·mol<sup>-1</sup> and energy barriers of  $E_a = 0.37$ , 0.36, and 0.44 kcal·mol<sup>-1</sup>, respectively. We notice that the intermediate state  $C_{2v}$  GS' (5) lies 0.08 kcal·mol<sup>-1</sup> higher than its

counterpart  $C_1$  GS (5). It is also worth noticing that the transition states TSs of these complexes have systematically longer I···O distances than that in the corresponding ground states GS and GS' in Figure 1, indicating that the bifurcated I <  $O_2$ N interactions in TSs are systematically weaker than the linear I···O XBs in the GSs and GSs'. The GS  $\rightleftharpoons$  TS  $\rightleftharpoons$  GS' fluxional mechanisms of complexes (3), (4), and (5) are vividly demonstrated in their IRC scanning processes in Videos S3–S5, respectively.

Figure 2 shows the variations of the cohesive energies ( $E_{\rm coh}$ ) of both the ground states (black line) and transition states (red line) of complexes (2), (3), (4), and (5) with the number of XBs (*n*) in the systems. Interestingly and intriguingly, the cohesive energies of the ground states increase with the numbers of XBs in an almost perfectly linear relationship of  $E_{\rm coh} = 3.48n + 0.18$ , with the slope



**FIGURE 2** The cohesive energies ( $E_{coh}$ ) of the ground states (black) and transition states (red) of complexes (2), (3), (4), and (5) increase with the number of XBs (*n*) in the systems almost perfectly linearly in parallel lines, with the transition states possessing slightly lower cohesive energies than corresponding ground states.

corresponding to the average halogen bond energy per XB of  $E_{coh/}$ <sub>XB</sub> = 3.48 kcal·mol<sup>-1</sup>. As anticipated, the cohesive energies of the transition states in Figure 2 vary in an almost parallel line  $E_{coh} = 3.47n$  – 0.18 which lies slightly lower than that of the corresponding ground states due to existence of a weaker van der Waals interaction in the transition states. The average halogen bond energy in complexes (2)–(5) appears to be about 55% of the average hydrogen bond energy ( $E_{coh/HB} = 6.28 \text{ kcal·mol}^{-1}$ ) in small water clusters (H<sub>2</sub>O)<sub>n</sub> (n = 2-9).<sup>30</sup>

The calculated ESP surface of the ground state (IC<sub>6</sub>F<sub>4</sub>I) (OONC<sub>6</sub>H<sub>4</sub>NOO) (2) in Figure 3 show obviously a positive  $\sigma$ -hole on the iodine atom (I3) in C<sub>s</sub> GS (2). Such a  $\sigma$ -hole accepts partial lonepair electrons from the negatively charged oxygen atom (O1), forming a 3c-2e linear halogen bond with the C–I···O bond angle close to 180°. In the bifurcated transition state C<sub>2v</sub> TS (2), the  $\sigma$ -hole on I3 interacts with two negatively charged oxygen atoms (O1, O2) simultaneously, but with obviously longer I···O distances (3.28 Å) than the corresponding value (3.08 Å) in GS (2)/GS' (2), making the transition state TS (2) 0.37 kcal·mol<sup>-1</sup> less stable than the ground states GS (2)/ GS' (2). The calculated ESP surfaces of complexes (3), (4), and (5) in Figures 3 and S2 show similar linear C–I···O XBs in their ground states and a bifurcated C–I < O<sub>2</sub>N van der Waals interaction in the corresponding transition states.

## 3.2 | Donor-acceptor orbital overlapping patterns

Detailed natural bond orbital (NBO) analyses were performed to unveil the orbital-overlap bonding patterns of the concerned complexes using the second-order perturbation theory of Fock matrix. In this approach, the stabilization energies (*E*(2)) are used to estimate the strengths of donor-acceptor interactions.<sup>66</sup> The interactions lead to loss of occupancy from the localized Lewis NBOs (bond or lone pair) into the empty non-Lewis NBOs (anti-bond or Rydberg) which stabilize the donoraccepter non-covalent interactions. The stabilization energies (*E*(2)) and the donor-acceptor orbital-overlap bonding patterns of the complexes (2), (3), (4), and (5) are shown in Figures 4 and S3–S5.



**FIGURE 3** Calculated electrostatic potential surfaces of the GSs, TSs and GSs' of (A) (IC<sub>6</sub>F<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) (**2**) and (B) (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (**3**), with the isosurface of electron density  $\rho = 0.07$  a.u. Blue color marks electron depleted areas and red color represents electron accumulated areas in a.u.

The linear XB in  $C_s$  GS (2) is mainly the interaction between the lone pair (LP) on O1 and the  $\sigma$ -anti-bonding orbital BD\*(I3-C4) which can be viewed as a 3c-2e XB with the stabilization energy of E(2)= 3.00 kcal·mol<sup>-1</sup>, as indicated in Figure 4A. When  $C_s$  GS (2) fluctuates to the bifurcated transition state  $C_{2v}$  TS (2), the 3c-2e XB in the GS (2) is transformed into a 4c-2e van der Waals interaction which represents mainly the interaction between the LPs of both O1 and O2 and the  $\sigma$ -anti-bonding orbital BD\*(I3-C4) with a slightly lower stabilization energy of  $E(2) = 1.44 \times 2 = 2.88$  kcal·mol<sup>-1</sup>.

As shown in Figure 4B–D, similar orbital overlapping patterns exist for the FXBs in complexes (3), (4), and (5). The stabilization energies E(2)= 2.95, 3.05, and 2.86 kcal-mol<sup>-1</sup> of linear 3c-2e XBs in  $C_{2h}$  GS (3),  $C_s$  GS (4), and  $C_1$  GS (5) appear to be slightly higher than the corresponding values in the bifurcated 4c-2e van der Waals interactions in  $C_1$  TS (3),  $C_s$ 

(A)  $(IC_6F_4I)(OONC_6H_4NOO)$ 

 $C_s \text{ GS (2)}$ 3c-2e XB LP (O1)  $\rightarrow$  BD\* (I3-C4)  $E(2) = 3.00 \text{ kcal·mol}^{-1}$ 

(B)  $(IC_6F_4I)_2(OONC_6H_4NOO)$ 

$$-$$

 $C_{2h} \text{ GS (3)}$ 3c-2e XB LP (O1)  $\rightarrow$  BD\* (I3-C4)  $E(2) = 2.95 \text{ kcal·mol}^{-1}$ 

(C)  $(IC_6F_4I)_2(OONC_6H_4NOO)_2$ 



 $C_{\rm s} \text{ GS (4)}$ 3c-2e XB LP (O1)  $\rightarrow$  BD\* (I3-C4)  $E(2) = 3.05 \text{ kcal·mol}^{-1}$ 

## (D) $(IC_6F_4I)_3(OONC_6H_4NOO)_2$

 $C_1 \text{ GS (5)}$  3c-2e XB  $LP (O5) \rightarrow BD^* (I7\text{-}C8)$   $E(2) = 2.86 \text{ kcal·mol}^{-1}$ 



TS (4), and  $C_1$  TS (5) where E(2) = 1.42 + 1.37 = 2.79, 1.31 + 1.50 = 2.81, and 1.34 + 1.37 = 2.71 kcal·mol<sup>-1</sup>, respectively. The linear XBs in  $C_{2v}$  GS' (3),  $C_1$  GS' (4) and  $C_{2v}$  GS' (5) collectively shown in Figure S3 possess similar orbital overlapping patterns and stabilization energies with their corresponding GSs. In the GSs  $\Rightarrow$  TSs  $\Rightarrow$  GSs' flux-ional mechanisms of these complexes, only one FXB undergoes a 3c-2e XB (GS)  $\Rightarrow$  4c-2e van der Waals interaction (TS)  $\Rightarrow$  3c-2e XB (GS') process, while all the other linear XBs remain basically unchanged.

#### 3.3 | NCI-RDG analyses

The NCI-RDG method which enables the weak interactions to be graphically visualized has been widely used to identify the types of



 $C_{2v} \text{ TS (2)}$ 4c-2e van der Waals interaction LP (O1) + LP (O2)  $\rightarrow$  BD\* (I3-C4)  $E(2) = 1.44 \text{ kcal·mol}^{-1}$   $E(2) = 1.44 \text{ kcal·mol}^{-1}$ 



 $C_1$  TS (3) 4c-2e van der Waals interaction LP (O1) + LP (O2)  $\rightarrow$  BD\* (I3-C4) E(2) = 1.42 kcal·mol<sup>-1</sup> E(2) = 1.37 kcal·mol<sup>-1</sup>



 $C_s \text{ TS } (4)$ 4c-2e van der Waals interaction LP (O1) + LP (O2)  $\rightarrow$  BD\* (I3-C4)  $E(2) = 1.31 \text{ kcal·mol}^{-1}$   $E(2) = 1.50 \text{ kcal·mol}^{-1}$ 

 $C_1$  TS (5) 4c-2e van der Waals interaction LP (O5) + LP (O6)  $\rightarrow$  BD\* (I7-C8) E(2) = 1.34 kcal·mol<sup>-1</sup> E(2) = 1.37 kcal·mol<sup>-1</sup>

**FIGURE 4** Donor-acceptor orbital overlapping patterns of the FXBs in the GSs and TSs of (A)  $(IC_6F_4)(OONC_6H_4NOO)$  (2), (B)  $(IC_6F_4I)_2(OONC_6H_4NOO)$  (3), (C)  $(IC_6F_4I)_2(OONC_6H_4NOO)_2$  (4), and (D)  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$  (5), with the stabilization energies E(2)/kcal·mol<sup>-1</sup> calculated in NBO analyses indicated.



**FIGURE 5** Calculated RDG versus sign( $\lambda_2$ ) $\rho$  plots and color-filled RDG isosurfaces of the isolated fragments OONC<sub>6</sub>H<sub>4</sub>NOO (B, B') and IC<sub>6</sub>F<sub>4</sub>I (C, C') and that of the GSs, TSs, GSs' of (IC<sub>6</sub>F<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) (D–F, D'–F') and (IC<sub>6</sub>F<sub>4</sub>I)<sub>2</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO) (G–I, G'–I') in the GS  $\rightleftharpoons$  TS  $\rightleftharpoons$  GS<sup>'</sup> fluxional processes.

non-covalent interactions. Johnson et al. developed reduced density gradient (RDG) approach and defined RDG(r) in Equation (2)<sup>62</sup>

$$RDG(r) = \frac{1 |\nabla \rho(r)|}{2(3\pi^2)^{\frac{1}{3}} \rho(r)^{\frac{4}{3}}}$$
(2)

Different types of noncovalent interactions can be discerned according to the electron density multiplied by the sign of the second Hessian eigenvalue  $(\sin(\lambda_2)\rho)$ . As shown in Figure 5A,  $\operatorname{sign}(\lambda_2)\rho < 0$  identifies strong non-covalent attractive interactions like HBs and XBs in blue,  $\operatorname{sign}(\lambda_2)\rho \approx 0$  shows weak van der Waals interactions in green, while  $\operatorname{sign}(\lambda_2)\rho > 0$  represents strong repulsions such as steric effect in rings and cages in red.<sup>67</sup>

Detailed NCI-RDG analyses were performed on fragments OONC<sub>6</sub>H<sub>4</sub>NOO and IC<sub>6</sub>F<sub>4</sub>I separately in Figure 5B,C, respectively, with the deep green spike 1 around  $\sin(\lambda_2)\rho = -0.017$  a.u corresponding to the HBs between O atoms and H atoms in OONC<sub>6</sub>H<sub>4</sub>NOO and the light green spike 2 around  $\sin(\lambda_2)\rho = -0.01$  a.u representing XBs between F atoms and I atoms in IC<sub>6</sub>F<sub>4</sub>I. As shown in Figure 5D, the NCI-RDG plot of the ground state (IC<sub>6</sub>F<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) (2) exhibits four spikes labeled as 1, 2, 3, and 4, respectively. Based on the analyses presented above, spike 1 corresponds to the HBs between O atoms and H atoms in fragment OONC<sub>6</sub>H<sub>4</sub>NOO, spike 2 corresponds to the XBs between I atoms and F atoms in fragment IC<sub>6</sub>F<sub>4</sub>I. The remaining spike 3 and spike 4 are located at sin

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 $(\lambda_2)\rho = -0.015$  and -0.005 a.u, respectively. According to the color scale in Figure 5A, spike 3 corresponds to the deep green isosurface between C4-I3...O1 in Figure 5D' which represents an effective XB between LP(O1) and BD\*(I3-C4) in Figure 4A, while spike 4 corresponds to the light green RDG isosurface with the approximate C4-I3...O2 bond angle of 148.17° in Figure 5D' which belongs to a weak van der Waals interaction. In the bifurcated transition state  $C_{2v}$  TS (2), spike 3 and spike 4 have merged into spike 5 around -0.01 a.u in Figure 5E which corresponds to the green RDG isosurface on the bifurcated C4-I3 <  $O_2N$  in Figure 5E', indicating that the linear 3c-2e XB in  $C_s$  GS (2) has been transferred into a bifurcated 4c-2e van der Waals interaction (spike 5) in the  $C_{2v}$  TS (2). Interestingly, spike 3 and spike 4 appear again in GS' (2) in Figure 5F, showing that the FXB goes backward and forward via a weak 4c-2e van der Waals interaction state TS (2).

Similar to  $(IC_6F_4I)(OONC_6H_4NOO)$  (2), the  $(IC_6F_4I)_2(OONC_6H_4NOO)$ (3),  $(IC_6F_4I)_2(OONC_6H_4NOO)_2$  (4), and  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$  (5) all exhibit four spikes in their ground states GS (3), GS (4), and GS (5). However, as shown in Figures 5 and S6, TS (3), TS (4), and TS (5) all possess five spikes (1, 2, 3, 4, and 5), with one bifurcated C—I < O\_2N van der Waals interaction (spike 5), one, two, and three linear C—I…O XBs (spikes 3), and one, two, and three weak bent C—I…O van der Waals interactions (spike 4), respectively. The coexistence of linear XBs and bifurcated van der Waals interaction results in the five spikes in the transition states.

(A)  $(IC_6F_4I)(OONC_6H_4NOO)$ 





(B)  $(IC_6F_4I)_2(OONC_6H_4NOO)$ 



 $C_{2h}$  GS (3)

 $(C) (IC_6F_4I)_2(OONC_6H_4NOO)_2$ 



C<sub>s</sub> GS (4)

(D)  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$ 













**FIGURE 6** Calculated QTAIM graphs of the GSs and TSs of (A)  $(IC_6F_4I)(OONC_6H_4NOO)$  (2), (B)  $(IC_6F_4I)_2(OONC_6H_4NOO)$  (3), (C)  $(IC_6F_4I)_2(OONC_6H_4NOO)_2$  (4), and (D)  $(IC_6F_4I)_3(OONC_6H_4NOO)_2$  (5). Green balls represent bond critical points of the weak non-covalent interactions including XBs and van der Waals interactions, orange balls show bond critical points of normal covalent bonds, red balls stand for ring critical points, while orange lines demonstrate the bond paths.

#### 3.4 | QTAIM analyses

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To obtain more information about the locations and strengths of the XBs in the concerned species, we performed detailed QTAIM calculations<sup>63</sup> on complexes (2), (3), (4), and (5) in Figures 6 and S7. Bond critical points (BCPs) on the bond paths are defined at locations where the gradient of electron density  $\rho(r)$  vanishes between two atoms. Various topological parameters at the BCP can describe the halogen bond interaction quantitatively, such as electron density  $\rho(r)$ , Laplacian  $\nabla^2 \rho$ , and the total electronic energy density H(r) at BCP. The electron density  $\rho(r)$  can be used to determine the strength of bond, the larger the  $\rho(r)$ , the stronger the bond is.<sup>68</sup> In general, low values of  $\rho(r)$  and positive values of Laplacian  $\nabla^2 \rho$  characterize close-shell interaction.<sup>69</sup> The negative values of H(r) may indicate the partial covalent character of the interaction.<sup>70,71</sup>

As demonstrated in Figure 6, in the ground states of the complexes (2), (3), (4), and (5), in addition to the BCPs of covalent bonds highlighted in orange balls, there exist one, two, three, and four BCPs in green balls on the bond paths along C–I…O directions, respectively, evidencing the existence of effective XBs in the systems around the BCPs, while in the transition states in the regions where the bifurcated van der Waals interactions are located possess two almost equivalent BCPs on two bond paths on the bifurcated  $C-I < O_2N$ structures. As can be seen from the topology parameters of corresponding BCPs of FXBs in complexes (2)-(5) tabulated in Table S1, the values of  $\rho(r)$  range from 0.009 to 0.014 a.u and the  $\bigtriangledown^2 \rho$  values are all positive, indicating the FXBs involved all belong to close-shell interactions.<sup>69</sup> The  $\rho(r)$  values in both GSs and GSs' are larger than the corresponding values in the TSs, indicating that the XBs in both the GSs and GSs' are stronger than the van der Waals interactions in the TSs,<sup>68</sup> in consistent with the NBO and NCI-RDG analyses presented above. The positive kinetic energy densities G(r) and the negative potential energy densities V(r) lead to a total energy density H(r) close to 0 in complexes (2)-(5), indicating that the XBs in these complexes belong to weak closed-shell contacts.<sup>71</sup>

# 4 | CONCLUSIONS

Based on detailed ESP, NBO, NCI-RDG, and QTAIM analyses, we unveil the existence of FXBs in linear (IC<sub>6</sub>H<sub>4</sub>I)(OONC<sub>6</sub>H<sub>4</sub>NOO) (1) and (IC<sub>6</sub>F<sub>4</sub>I)<sub>m</sub>(OONC<sub>6</sub>H<sub>4</sub>NOO)<sub>n</sub> (2)–(5) (m + n = 2-5) which contain up to four XBs in this work. The fluxional mechanisms GS  $\Rightarrow$  TS  $\Rightarrow$  GS' of XBs appear to be similar to that of the fluxional hydrogen bonds in small water clusters (H<sub>2</sub>O)<sub>n</sub> (n=2-6), with one linear C–I···O XB in the GS fluctuating reversibly via a bifurcated C–I < O<sub>2</sub>N van der Waals interaction in the TS to a similar linear C–I···O XB in GS', facilitating the structural fluxionality of the systems. The cohesive energies of these complexes increase with the number of XBs almost perfectly linearly, indicating that the XBs in the systems behave almost independently. The extension of fluxional bonds from intramolecular fluxional covalent bonds, intermolecular fluxional hydrogen bonds, to intermolecular FXBs in the structural fluxional

processes from one ground state through a transition state to another ground state may have important applications in molecular dynamics, molecular assembling, and crystal engineering. FXBs are anticipated to play an important role in supramolecules, biomolecules, and may even be involved in phase transitions in molecular crystals.

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#### CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

#### DATA AVAILABILITY STATEMENT

the data is available according to JCC policies.

#### ORCID

Si-Dian Li D https://orcid.org/0000-0001-5666-0591

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