

Non-monotonic Structure-Property Relationships in Small Iron-Doped Boron Clusters: A DFT Study of B_nFe (n = 3-6)

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Abstract

Context

Small iron-doped boron clusters are useful model systems for examining how structure, excited-state behavior, and chemical reactivity evolve at low nuclearity. Here, the neutral B_nFe series ($n = 3-6$) was studied to determine whether increasing boron content yields a simple size-dependent progression or instead leads to distinct mechanistic regimes. The results reveal a clearly non-monotonic evolution, with B_4Fe emerging as the most mechanistically transparent molecular-activation prototype, B_3Fe defining a dissociative activation limit, and B_6Fe representing the global softness/electrophilicity limit.

Methods

The B_nFe clusters were investigated using an integrated density functional theory workflow combining ground-state optimization, harmonic vibrational analysis, selected-state TDDFT calculations, natural transition orbital analysis, global conceptual-DFT descriptors, condensed Fukui functions, and a prototype H_2 -activation test. The optimized PBE0/def2-TZVP structures confirmed stable minima and showed a non-monotonic structural trend: B_3Fe is compact and planar, B_4Fe is non-planar but relatively rigid, B_5Fe is the most distorted and vibrationally soft member, and B_6Fe regains partial compactness while remaining non-planar. Optical analysis showed that B_4Fe and B_5Fe absorb at similar low energies, but B_4Fe is much brighter and more coherent. Global descriptors identified B_6Fe as the softest and most electrophilic cluster, whereas local Fukui analysis showed that B_4Fe provides the clearest Fe/B reactivity differentiation. In the H_2 -interaction analysis, B_3Fe yielded a dissociative or near-dissociative product, whereas B_4Fe - B_6Fe retained molecular H_2 adducts, with B_4Fe showing the strongest geometric activation of the H-H bond.

1 Introduction

Boron-based clusters have long attracted attention in molecular modeling because they often behave very differently from conventional main-group systems. Owing to their electron-deficient character, boron aggregates frequently stabilize through multicenter bonding, unusual geometries, and highly size-sensitive electronic structures, making them valuable model systems for examining how bonding, stability, and reactivity evolve at the nanoscale [1, 13, 14]. This already rich chemistry becomes even more interesting when a transition metal is incorporated into the boron framework.

Among possible dopants, iron is particularly attractive because it contributes not only valence d orbitals, but also a flexible coordination environment capable of reshaping the bonding topology of small boron clusters. Earlier studies have shown that Fe-containing boron systems can stabilize unconventional motifs, including planar or quasi-planar arrangements that are difficult to rationalize using simple classical bonding ideas [1, 2, 15, 16]. Beyond isolated molecular species, Fe-B architectures have also attracted increasing interest in cluster-derived materials due to their unusual electronic, magnetic, and potentially functional properties [2, 3, 15, 17]. These findings suggest that even small Fe-doped boron clusters may already capture chemically meaningful trends relevant to both fundamental bonding theory and future materials design.

Despite this growing literature, the behavior of small neutral B_nFe clusters remains insufficiently clarified when examined as a connected size series. In particular, the progression from B_3Fe to B_6Fe cannot simply be assumed to be monotonic. Adding a single boron atom does not necessarily lead to a straightforward increase in stability, softness, optical accessibility, or activation capability. In small cluster chemistry, a single-atom increase can reorganize the entire framework, alter Fe-B coupling, and shift the balance between framework-dominated and metal-centered reactivity. This is precisely why a comparative study of B_3Fe - B_6Fe is valuable: it allows one to examine how subtle size changes generate qualitatively different chemical behavior rather than merely quantitative variation [13, 16–18].

This issue is especially important from a density functional theory perspective. DFT has become a central tool for interpreting the structure, energetics, spectroscopy, and reactivity of molecular and cluster systems, but meaningful conclusions usually emerge only when several descriptors are read together rather than in isolation [4, 19, 20]. A system that appears most reactive from global softness, for example, may not necessarily be the one that exhibits the clearest local electrophilic site, the most coherent excited-state response, or the strongest geometric signature of bond activation. For this reason, a reliable interpretation of Fe-doped boron clusters should not depend on a single metric. Instead, it should integrate structural stability, excited-state characteristics, global conceptual-DFT descriptors, local Fukui reactivity, and a chemically explicit activation probe.

The present study addresses this gap through an integrated DFT-based investigation of the B_nFe series ($n = 3-6$). Rather than treating structure, optics, and reactivity as separate themes, this work approaches them as interconnected dimensions of the same chemical problem. The analysis is organized around four complementary axes: structural characterization of optimized minima, electronic and optical behavior from selected excited states, global and local reactivity descriptors derived from conceptual DFT, and a prototype H_2 -interaction assessment to test how the clusters translate descriptor-based tendencies into an explicit activation scenario. This multi-axis framework is important because it allows the

chemically most informative member of the series to be identified not merely by one extreme value, but by convergence across several independent indicators.

A central premise of this manuscript is that small Fe-doped boron clusters exhibit a non-monotonic size-property relationship. In other words, the chemically most significant cluster is not automatically the largest one, the softest one, or the one with the lowest excitation energy. Instead, the B_nFe series appears to evolve through a competition between structural distortion, metal-framework cooperation, and electronically accessible reactive channels. Within such a landscape, one cluster may be globally softer, another may be optically brighter, and yet another may offer the clearest local separation between electron donation and acceptance. This makes the series particularly suitable for probing a broader mechanistic question: which descriptor, or combination of descriptors, best identifies a genuinely informative reactive prototype?

2 Computational Methods

2.1 Ground-state geometry optimization and vibrational analysis

The structural reference for the B_nFe series was established from full geometry optimizations followed by harmonic vibrational frequency calculations at the PBE0/def2-TZVP level. The PBE0 hybrid functional was chosen because it is a non-empirical hybrid model that has shown balanced performance for molecular structures, energetics, and related properties [5]. The def2-TZVP basis set was selected as a practical triple-zeta basis of broadly validated accuracy for molecular calculations involving both main-group and transition-metal elements [6].

All optimized structures were verified by harmonic frequency analysis to ensure they correspond to genuine local minima on the potential energy surface. In the final reoptimized dataset, B_3Fe , B_4Fe , B_5Fe , and B_6Fe all showed zero imaginary frequencies, confirming that all four clusters are true minima at the present level of theory. The vibrational results also provided additional information on structural softness. Whereas B_4Fe showed no positive modes below 200 cm^{-1} , B_3Fe , B_5Fe , and B_6Fe retained low-frequency positive modes, indicating a higher degree of vibrational compliance within those frameworks. In particular, B_5Fe exhibited the richest low-frequency pattern, consistent with a comparatively soft and deformable potential energy surface. This structural and vibrational layer, therefore, serves as the most secure reference frame for the rest of the manuscript.

2.2 Excited-state calculations and NTO analysis

The electronic and optical properties of the B_nFe clusters were examined using linear-response TDDFT within the Tamm-Dancoff approximation and the $\omega B97X-D$ functional. TDDFT/TDA was employed because it offers an efficient framework for exploring low-lying excited states while often providing numerically stable results for open-shell or delicate excited-state problems [7]. The use of $\omega B97X-D$ was motivated by its long-range-corrected form combined with empirical dispersion, which has been shown to perform well across a broad range of thermochemical, kinetic, and noncovalent applications [8].

For each cluster, one target excited state was selected as the principal interpretive state based on excitation energy, oscillator strength, and the clarity of the underlying transition pattern. The selected states were state 15 for B_3Fe , state 10 for B_4Fe , state 8 for B_5Fe , and state 10 for B_6Fe .

To interpret the electronic transitions in a compact and chemically transparent way, the excited-state analysis was complemented by natural transition orbitals. NTOs provide a reduced representation of the transition density and are especially useful when a conventional orbital-amplitude description becomes diffuse or distributed over many configurations [9]. In the present work, the official excitation energies were always taken from the main excited-state summary blocks of the output files. In contrast, the NTO analysis was used qualitatively to describe hole-particle compactness, spin balance, and dominant excitation channels.

2.3 Global conceptual-DFT descriptors

Global reactivity trends were evaluated using finite-difference conceptual-DFT descriptors derived from the neutral, cationic, and anionic states of each cluster. The quantities considered were the ionization energy (I), electron affinity (A), electronegativity (χ), chemical potential (μ), hardness (η), softness (S), and electrophilicity index (ω). The electrophilicity index used here follows the conceptual-DFT formalism introduced by Parr and co-workers [10], while the broader descriptor framework is consistent with modern conceptual-DFT treatments of molecular reactivity [19, 20]. The same finite-difference protocol was applied consistently to all four members of the series, allowing a direct internal comparison of the global reactivity landscape.

2.4 Condensed Fukui functions and local reactivity analysis

To complement the global descriptors, local reactivity was examined using condensed Fukui functions. In practical terms, these quantities were obtained from atomic population changes between the neutral, cationic, and anionic states, following the standard atom-condensed finite-difference framework introduced for local site analysis [11, 19]. In the present study, the condensed descriptors were built from Mulliken net atomic charges.

The resulting f_k^+ , f_k^- , and f_k^0 values were then used to identify preferred sites for electron acceptance, electron donation, and radical-type response, respectively. At the same time, these local descriptors were interpreted with appropriate caution, since condensed Fukui values can depend on the underlying population scheme, and Mulliken-based forms are known to be sensitive in absolute terms [12, 19, 20]. For that reason, the local Fukui analysis was used primarily here to compare how redistribution of reactivity between Fe and the boron framework occurs within the same internally consistent protocol.

2.5 Prototype H₂ binding and activation test

To connect the descriptor-based picture to a more explicit chemical probe, a prototype H₂-binding test was performed for all four clusters. The purpose of this step was not yet to establish final adsorption thermodynamics, but to determine whether the clusters could support molecular H₂ binding or induce deeper bond activation under geometry optimization.

The optimized interaction geometries were analyzed mainly in terms of the H-H distance, Fe-H distances, and the corresponding raw electronic interaction energies evaluated relative to the optimized bare cluster and free H₂. These quantities were treated as screening-level indicators rather than final adsorption observables, since zero-point, thermal, BSSE, and deeper spin-state refinements were not included at this stage.

2.6 Validation strategy and scope of interpretation

Because the B_nFe series includes open-shell species and not all properties were evaluated to the same theoretical level, the final interpretation was based on a simple validation hierarchy. The structural conclusions are considered the most reliable because they rest on a uniform optimization-and-frequency protocol at the PBE0/def2-TZVP level and are supported by the absence of imaginary frequencies for all four clusters. The excited-state results are chemically informative but remain more sensitive to state following and spin quality in some cases. The global conceptual-DFT descriptors are robust for comparative intra-series trends, whereas the local Fukui results should be interpreted with caution given their dependence on Mulliken population analysis. Finally, the H₂-binding calculations are already useful for identifying promising activation motifs, but they remain preliminary at the energetic level.

3 Results and Discussion

3.1 Structural features and size-dependent stability of the B_nFe series

The optimized ground-state geometries of the B_nFe clusters are shown in Fig. 1, while the main structural metrics are summarized in Table 1. Harmonic vibrational analysis further confirmed that all four systems, namely B₃Fe, B₄Fe, B₅Fe, and B₆Fe, are true local minima, since no imaginary frequencies were found in the final reoptimized frequency calculations. This point is important because it establishes a firm structural basis for the subsequent discussion of optical and reactivity. At the same time, the geometries and vibrational patterns show that the structural evolution of the series is distinctly non-monotonic. Rather than becoming progressively more regular or more distorted with increasing boron nuclearity, each cluster adopts a distinct compromise among Fe coordination, boron-framework organization, and vibrational flexibility.

Table 1
Structural summary of the B_nFe series at the PBE0/def2-TZVP level.

Cluster	Multiplicity	Imaginary frequencies	Fe–B min (Å)	Fe–B max (Å)	B–B min (Å)	B–B max (Å)	All-atom RMS planarity (Å)	B-framework RMS planarity (Å)	Ground-state description	Structural interpretation
B ₃ Fe	2	0	1.7087	1.7087	2.9594	2.9600	0.0000	0.0000	planar compact doublet	compact, symmetric triangular FeB3 motif
B ₄ Fe	1	0	1.7581	1.7586	2.8697	2.8728	0.9074	1.0145	pyramidal/open singlet	larger but clearly non-planar FeB4 coordination environment
B ₅ Fe	4	0	1.8354	2.3413	1.5653	4.1053	0.4926	0.5396	distorted open-shell minimum	widest Fe–B spread; most distorted framework
B ₆ Fe	3	0	1.7758	1.8628	2.5376	3.7241	0.9556	1.0321	compact but non-planar open-shell minimum	regains narrower Fe–B range relative to B5Fe

The smallest member, B₃Fe, corresponds to a remarkably compact and planar doublet. As shown in Fig. 1, the Fe atom and the three boron atoms form a highly symmetric FeB₃ motif, and the extracted structural parameters in Table 1 confirm this visual impression. The Fe-B distances are identical within numerical precision, and the all-atom as well as boron-framework RMS planarity values are essentially zero. Even so, the frequency calculation still shows two low positive modes below 200 cm⁻¹, indicating that B₃Fe, while highly regular and planar, is not completely rigid. Structurally, B₃Fe can therefore be described as the most compact and symmetric cluster in the series, but still one that retains some degree of low-frequency compliance.

A different picture emerges for B₄Fe. Although one might expect the addition of a fourth boron atom to preserve or even extend the compact regularity of B₃Fe, the optimized structure instead becomes clearly non-planar. The extracted RMS planarity values in Table 1 show a substantial departure from planarity, even though the Fe-B distance range itself remains narrow. This means that the structural change from B₃Fe to B₄Fe is not dominated by strong bond-length differentiation, but by a reorganization of the three-dimensional framework. At the same time, the vibrational result for B₄Fe is notable because it shows no positive modes below 200 cm⁻¹. In this sense, B₄Fe is the most structurally rigid member of the series, despite not being planar. It therefore combines geometric reorganization with an unexpectedly firm vibrational profile.

The distortion becomes much more pronounced in B₅Fe, which is structurally the most heterogeneous member of the series. As seen in Fig. 1, the framework no longer preserves the compact geometric simplicity of B₃Fe or the relatively controlled non-planarity of B₄Fe. Instead, B₅Fe exhibits the broadest Fe-B distance distribution together with the widest spread of B-B distances in the set. This makes B₅Fe the clearest example of structural frustration in the present series. The vibrational data reinforce this interpretation: B₅Fe displays four positive modes below 200 cm⁻¹, the richest low-frequency pattern among the four clusters. Thus, B₅Fe is not only the most distorted structure geometrically, but also the softest one vibrationally. The addition of the fifth boron atom, therefore, introduces a particularly compliant and weakly regularized structural regime.

For B₆Fe, the geometry remains non-planar, but the structure becomes more compact again relative to B₅Fe. This is an important result because it shows that the distortion trend does not simply intensify with cluster size. Instead, B₆Fe regains a narrower Fe-B distance interval than B₅Fe, suggesting that the six-boron framework is able to reorganize into a somewhat more balanced coordination pattern. Even so, the vibrational analysis still reveals three low positive modes below 200 cm⁻¹, indicating that the regained compactness does not correspond to a rigid structural endpoint. B₆Fe therefore represents a partially restabilized but still vibrationally compliant non-planar structure.

Taken together, the structural results show that the B_nFe series does not follow a simple size-dependent progression. B₃Fe is the most planar and symmetric structure; B₄Fe introduces clear non-planarity but is the most rigid vibrationally, B₅Fe is the most distorted and vibrationally soft system, and B₆Fe becomes more compact again while retaining non-planarity and moderate structural softness. This sequence is important because it establishes the first major theme of the manuscript: structural growth in small Fe-doped boron clusters is governed not by linear regularization but by repeated geometric reorganization accompanied by changes in vibrational flexibility [13, 15].

3.2 Electronic and optical behavior of the selected excited states

The selected excited-state properties of the B_nFe clusters are summarized in Table 2, while the comparative trends in excitation energy and oscillator strength are shown in Fig. 2. The schematic NTO contribution profiles are presented in Fig. 3. Taken together, these results show that the optical behavior of the series is as non-monotonic as its structural evolution. Increasing boron nuclearity does not lead to a simple red shift, a progressive increase in intensity, or a systematic improvement in excited-state coherence.

Table 2
Selected excited-state properties of B_nFe clusters from TDDFT/TDA calculations.

Cluster	Selected state	Excitation energy (eV)	Wavelength (nm)	Oscillator strength	<S^2>	Dominant NTO character	Optical interpretation
B3Fe	15	2.4519	505.7	0.00417	2.9704	two dominant α pairs (39.8%, 39.4%)	higher-energy, distributed excitation
B4Fe	10	1.6906	733.5	0.02641	0.0000	balanced α/β pair (49.5%, 49.5%)	brightest and most coherent
B5Fe	8	1.6939	732.0	0.00693	4.7461	β-dominated single-pair excitation (92.5%)	low-energy but spin-polarized
B6Fe	10	1.9328	641.6	0.00139	3.9640	mixed and fragmented; β-dominant	weak and fragmented

Among the four clusters, B₃Fe corresponds to the highest-energy selected excitation. Its target state appears at 2.4519 eV (505.7 nm) with a relatively small oscillator strength of 0.00417. In energetic terms, B₃Fe is therefore clearly separated from the other three clusters, which all

absorb at lower energies. The NTO profile in Fig. 3 further shows that the B₃Fe excitation is not dominated by a single compact transition channel.

A sharply different behavior is found for B₄Fe, which emerges as the clearest optical reference point of the series. Its selected excitation occurs at 1.6906 eV (733.5 nm), making it one of the lowest-energy transitions in the set, but its most striking feature is its much larger oscillator strength of 0.02641. As shown in Fig. 2, this makes B₄Fe by far the brightest member of the B₃Fe-B₆Fe series.

B₅Fe occupies an especially instructive intermediate position. Its selected excited state lies at 1.6939 eV (732.0 nm), which is essentially identical in energy to B₄Fe. However, this near-equality in excitation energy does not translate into equivalent optical behavior. The oscillator strength of B₅Fe drops to 0.00693, much lower than that of B₄Fe, and a single beta-spin contribution strongly dominates the NTO profile.

For B₆Fe, the selected excitation is found at 1.9328 eV (641.6 nm), placing it energetically between B₃Fe and the B₄Fe/B₅Fe pair. However, B₆Fe exhibits the smallest oscillator strength of the series, only 0.00139, indicating that this transition is only weakly allowed. The NTO profile also shows a more fragmented contribution pattern than in B₄Fe or B₅Fe.

When the four systems are compared together, the most important outcome is that the optical response does not scale directly with cluster size. The selected excitation energies follow the order B₄Fe $\approx$ B₅Fe < B₆Fe < B₃Fe, whereas the oscillator strengths follow B₄Fe > B₅Fe > B₃Fe > B₆Fe. From this perspective, B₄Fe clearly stands out as the optical anchor of the B_nFe series.

3.3 Global and local reactivity of the B_nFe clusters

The global conceptual-DFT descriptors of the B_nFe series are summarized in Table 3, and their comparative trends are illustrated in Fig. 4. Taken together, these data show that the global reactivity of the series is also distinctly non-monotonic. The descriptors do not support a simple size-based interpretation in which progressively larger clusters become progressively softer or more reactive in a uniform way [19, 20].

Table 3
Global conceptual-DFT descriptors of the B_nFe clusters.

Cluster	I (eV)	A (eV)	χ (eV)	μ (eV)	η (eV)	S (eV ⁻¹)	ω (eV)
B3Fe	8.0756	1.6112	4.8434	-4.8434	3.2322	0.1547	3.6289
B4Fe	7.4767	2.2972	4.8870	-4.8870	2.5898	0.1931	4.6109
B5Fe	7.8199	1.8234	4.8217	-4.8217	2.9983	0.1668	3.8770
B6Fe	7.2492	2.5344	4.8918	-4.8918	2.3574	0.2121	5.0755

Table 4
Condensed Fukui functions for the key Fe and B sites in B_nFe clusters.

Cluster	Site	f _k ⁺	f _k ⁻	f _k ⁰	Local interpretation
B ₃ Fe	Fe	0.0032	-0.0070	-0.0019	Fe nearly silent locally
B ₃ Fe	B ₄	0.3684	0.3356	0.3520	strongest all-around hotspot
B ₃ Fe	B ₂	0.3142	0.3357	0.3249	boron-led donor/reactive site
B ₃ Fe	B ₃	0.3142	0.3357	0.3249	boron-led donor/reactive site
B ₄ Fe	Fe	0.2901	0.1086	0.1994	main electron-accepting site
B ₄ Fe	B ₄	0.1334	0.2922	0.2128	main electron-donating/radical site
B ₄ Fe	B ₅	0.1333	0.2922	0.2128	main electron-donating/radical site
B ₄ Fe	B ₃	0.2730	0.1094	0.1912	secondary accepting site
B ₅ Fe	Fe	0.0425	0.0578	0.0501	minor local role
B ₅ Fe	B ₂	0.4592	0.2537	0.3564	dominant hotspot
B ₅ Fe	B ₄	0.2056	0.1978	0.2017	secondary reactive site
B ₅ Fe	B ₅	0.2056	0.1978	0.2017	secondary reactive site
B ₆ Fe	Fe	0.1980	0.0107	0.1044	important for f ⁺ , weak for f ⁻
B ₆ Fe	B ₃	0.1927	0.1148	0.1538	shared accepting site
B ₆ Fe	B ₆	0.1892	0.1689	0.1790	main radical hotspot
B ₆ Fe	B ₂ /B ₄ /B ₅ /B ₇	0.1050	0.1764	0.1407	boron-led donation pattern

From the perspective of the global descriptor, B₆Fe is the most reactive member of the series. It has the lowest chemical hardness, the highest softness, and the largest electrophilicity index among the four clusters. In contrast, B₃Fe lies at the opposite end of the spectrum, with the highest hardness and the lowest softness. B₄Fe and B₅Fe occupy intermediate positions, although B₄Fe is clearly softer and more electrophilic than B₅Fe.

However, the local reactivity pattern reveals a more differentiated picture. The condensed Fukui functions for the key Fe and B sites are given in Table 4. Rather than uniformly reinforcing the global ranking, these local descriptors show that different clusters distribute reactivity between the Fe center and the boron framework in very different ways, which is fully consistent with the broader conceptual-DFT expectation that global and local indices need not privilege the same reactive prototype [19, 20].

In B₃Fe, the Fe center is almost locally silent, whereas the dominant reactive sites are located on the boron atoms. In B₄Fe, the Fe atom becomes the principal site for electron acceptance, whereas specific boron atoms dominate the electron-donating and radical channels. In other words, B₄Fe shows the clearest functional separation between Fe-centered electrophilic behavior and boron-centered donor or radical activity.

For B₅Fe, the local reactivity shifts back toward boron dominance. In B₆Fe, the local picture becomes more mixed: the Fe site contributes significantly to f_k⁺, but the boron framework still dominates much of the donation and radical response. When the global and local descriptors are read together, a more nuanced mechanistic picture emerges. B₆Fe is the most reactive cluster in global conceptual-DFT terms, but B₄Fe is the most chemically transparent cluster in local terms.

3.4 Prototype H₂ activation in the B_nFe series

The optimized H₂-interaction structures derived from the uploaded output files are shown in Fig. 6, and the corresponding geometric and electronic indicators are summarized in Table 5. Once again, the results reveal a distinctly non-uniform behavior across the B_nFe series. Rather than following a single activation motif, the four clusters separate into two mechanistic regimes: one dissociative and the other molecular.

Table 5
Geometric and electronic indicators of H₂ activation in the B_nFe series.

Cluster	Multiplicity	Complex energy (Eh)	E _{bind} (Eh)	E _{bind} (kcal mol ⁻¹)	H-H (Å)	Fe-H1 (Å)	Fe-H2 (Å)	Binding mode	Mechanistic interpretation
B3Fe	2	-1339.038990	-0.337807	-211.98	2.058	1.847	3.134	dissociative or near-dissociative H ₂ activation product	dissociative or near-dissociative activation
B4Fe	1	-1363.737832	-0.301173	-188.99	0.880	1.661	1.596	activated molecular H ₂ adduct	strongest molecular H ₂ activation
B5Fe	4	-1388.597470	-0.201358	-126.35	0.797	1.828	1.828	activated molecular H ₂ adduct	moderate molecular activation
B6Fe	3	-1413.355874	-0.423145	-265.53	0.798	1.860	1.841	activated molecular H ₂ adduct	moderate molecular activation with stronger raw binding

The most striking result is obtained for B₃Fe. In this case, the optimized structure no longer corresponds to a molecularly bound H₂ adduct. Instead, the H-H distance increases to 2.058 Å, far beyond the range expected for an activated but intact dihydrogen ligand. This geometry is therefore best interpreted as a dissociative or near-dissociative H₂ activation product.

By contrast, B₄Fe, B₅Fe, and B₆Fe all preserve a molecularly bound H₂ unit, although with different degrees of activation. Among these three, B₄Fe-H₂ shows the clearest geometric signature of molecular activation. Its H-H bond is elongated to 0.880 Å, noticeably longer than those in B₅Fe-H₂ (0.797 Å) and B₆Fe-H₂ (0.798 Å). Thus, within the class of molecular H₂ adducts, B₄Fe remains the strongest prototype for activation.

The comparison between B₅Fe-H₂ and B₆Fe-H₂ is also informative. Both systems stabilize molecular adducts with only moderate H-H elongation, and both show longer Fe-H contacts than B₄Fe-H₂. However, the raw electronic binding energies indicate that B₆Fe-H₂ is more strongly stabilized than B₅Fe-H₂. This creates another instructive mismatch between energetic stabilization and geometric activation.

Taken together, the present H₂-activation analysis reveals two mechanistic motifs in the B_nFe series. B₃Fe represents a dissociative activation channel, whereas B₄Fe-B₆Fe belong to a molecular activation channel. Within the latter group, B₄Fe is the most compelling system because it gives the clearest geometric evidence of H-H activation while still preserving an intact molecular ligand. In this sense, the H₂-binding results reinforce the broader lesson that stronger raw electronic stabilization does not automatically identify the most mechanistically transparent reactive pattern [4, 19].

4 Conclusion

This study shows that the small iron-doped boron cluster series B_nFe (n = 3–6) is governed by a strongly non-monotonic structure-property relationship. Across the four analytical axes considered here, namely structure, excited-state behavior, conceptual-DFT reactivity, and H₂ activation, the addition of boron atoms does not produce a simple linear progression. Instead, each nuclearity defines a distinct balance between framework organization, Fe-B coupling, and chemically accessible reactive pathways.

At the structural level, B₃Fe forms a compact, planar limit; B₄Fe introduces a non-planar but relatively even Fe-B environment; B₅Fe represents the most distorted regime; and B₆Fe partially regains compactness while remaining non-planar. The optical analysis reveals a similarly nonlinear trend, with B₄Fe emerging as the brightest and most coherent selected excitation, B₃Fe remaining higher in energy and more distributed, B₅Fe becoming more spin-polarized, and B₆Fe showing weaker and more fragmented optical behavior.

The reactivity descriptors further refine this picture. Global conceptual-DFT indices identify B₆Fe as the softest and most electrophilic member of the series. In contrast, the condensed Fukui analysis shows that B₄Fe provides the clearest local separation between Fe-centered electron acceptance and boron-centered donor or radical activity. The H₂-interaction analysis confirms that these clusters do not share a single activation motif: B₃Fe proceeds toward dissociative or near-dissociative activation, whereas B₄Fe-B₆Fe stabilize molecular H₂ adducts, with B₄Fe showing the strongest geometric molecular activation.

Taken together, the present results demonstrate that no single descriptor is sufficient to identify the chemically most informative member of the B_nFe series. Although B₆Fe defines the global softness and electrophilicity limit, and B₃Fe represents a distinct dissociative activation channel,

B₄Fe emerges as the most mechanistically transparent molecular-activation prototype because structural, optical, local-reactivity, and H₂-activation evidence converge most clearly on this system. These findings provide a coherent basis for future refinement of Fe-doped boron clusters as model systems for size-dependent reactivity and activation chemistry.

Declarations

Ethics Approval and Consent to Participate

Not applicable (systematic review of published literature).

Consent for Publication

Not applicable.

Competing Interests

The authors declare no competing interests.

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Author Contribution

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Frans Augusthinus Asmuruf, Supeno, Ilham Salim, Yuliana Ruth Yabansabra, and Eva Susanty Simaremare. Frans Augusthinus Asmuruf wrote the first draft of the manuscript, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability

All data generated or analyzed during this study are included in this published article and its supplementary information files.

The datasets generated and analyzed during the current study are available in the supplementary materials associated with this article. Final optimized coordinates, selected output files, and numerical datasets underlying Tables 1–5 are provided as Online Resources.

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Figures

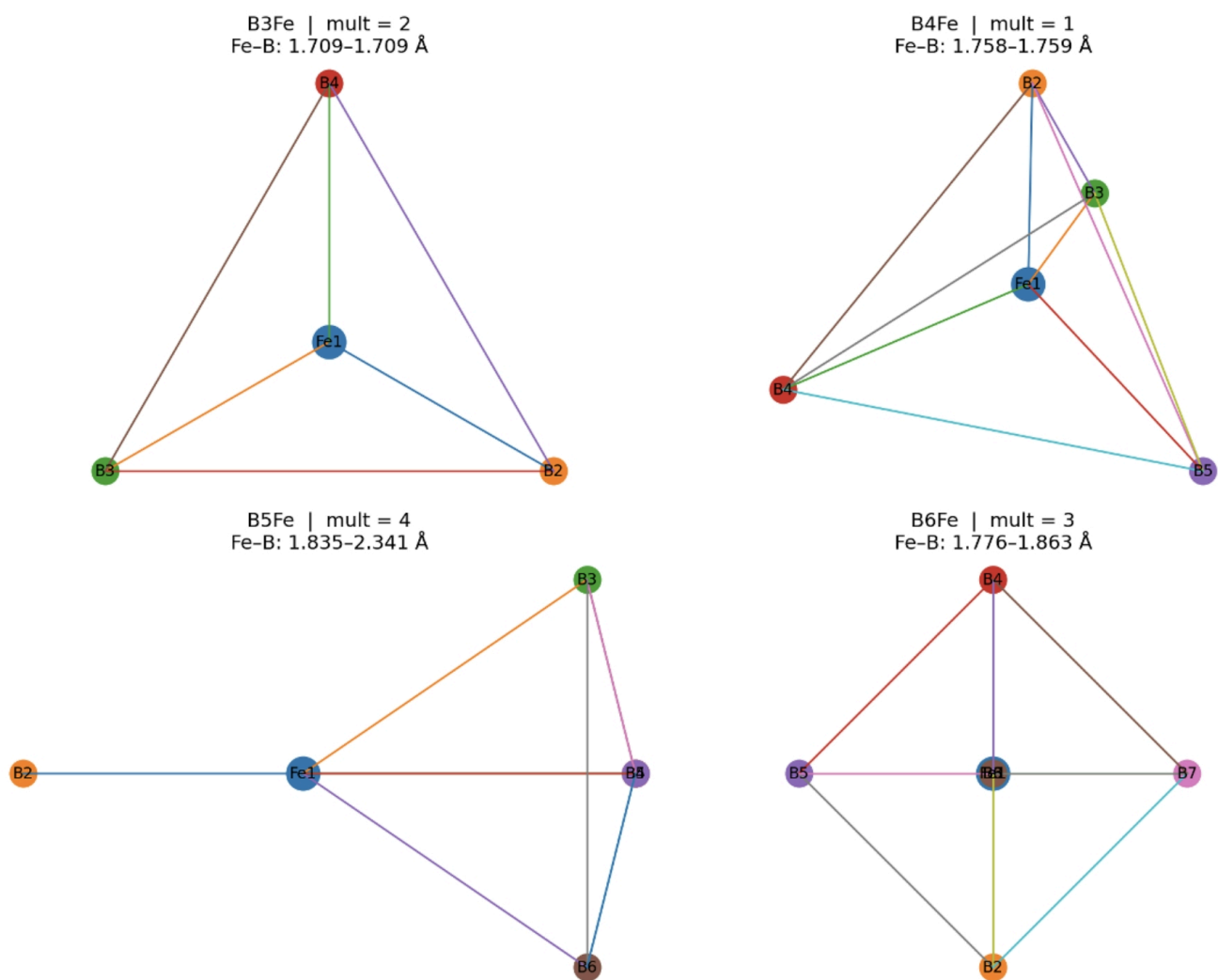


Figure 1

Optimized ground-state geometries of the $B_n\text{Fe}$ clusters ($n = 3-6$) obtained at the PBE0/def2-TZVP level.

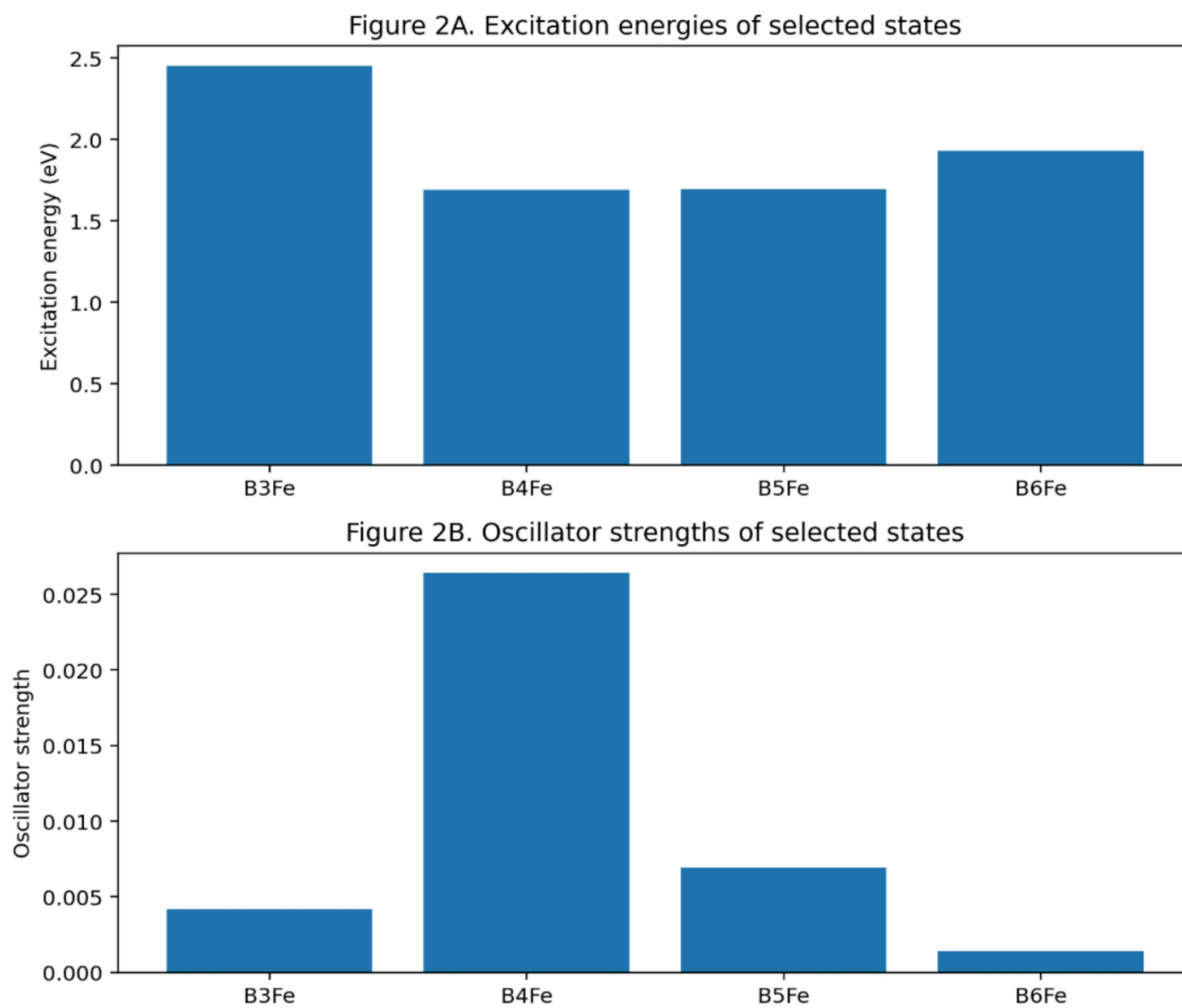


Figure 2

Comparative optical summary of the selected excited states in B_3Fe - B_6Fe : (A) excitation energies and (B) oscillator strengths.

Figure 3. Schematic NTO contribution profiles of the selected excited states

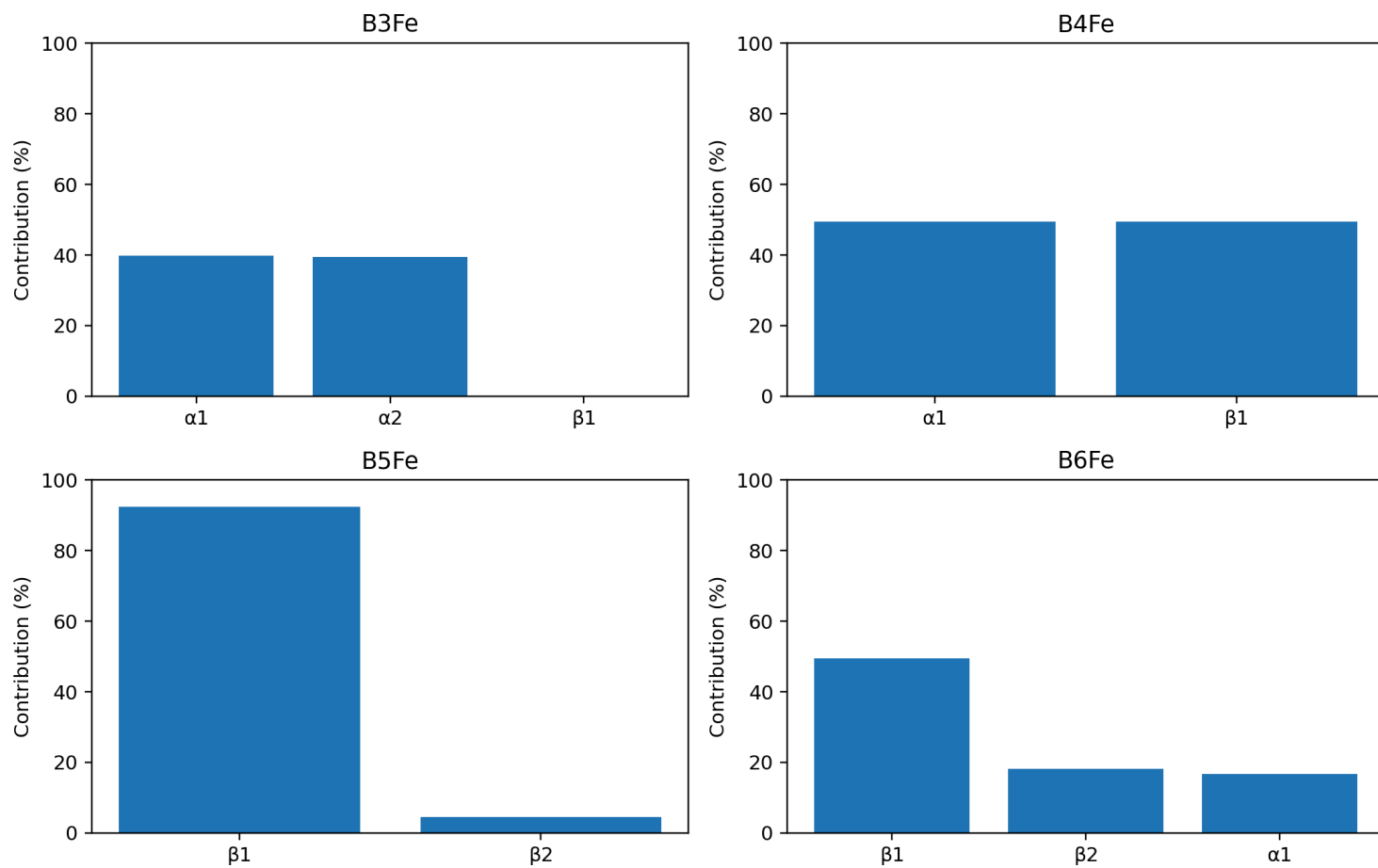


Figure 3

See image above for figure legend

Figure 4A. η (eV)

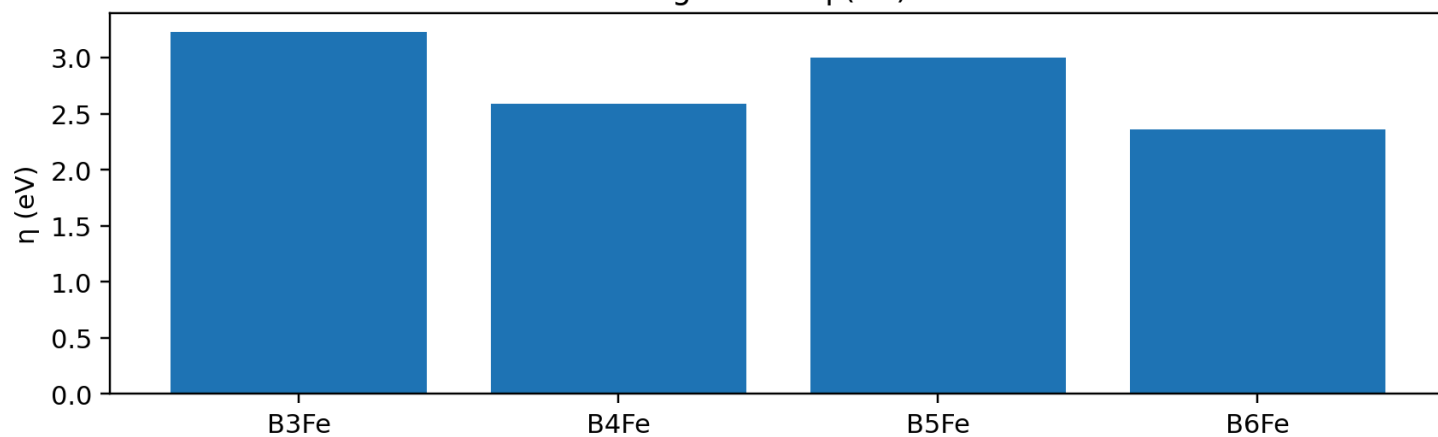


Figure 4B. S (eV⁻¹)

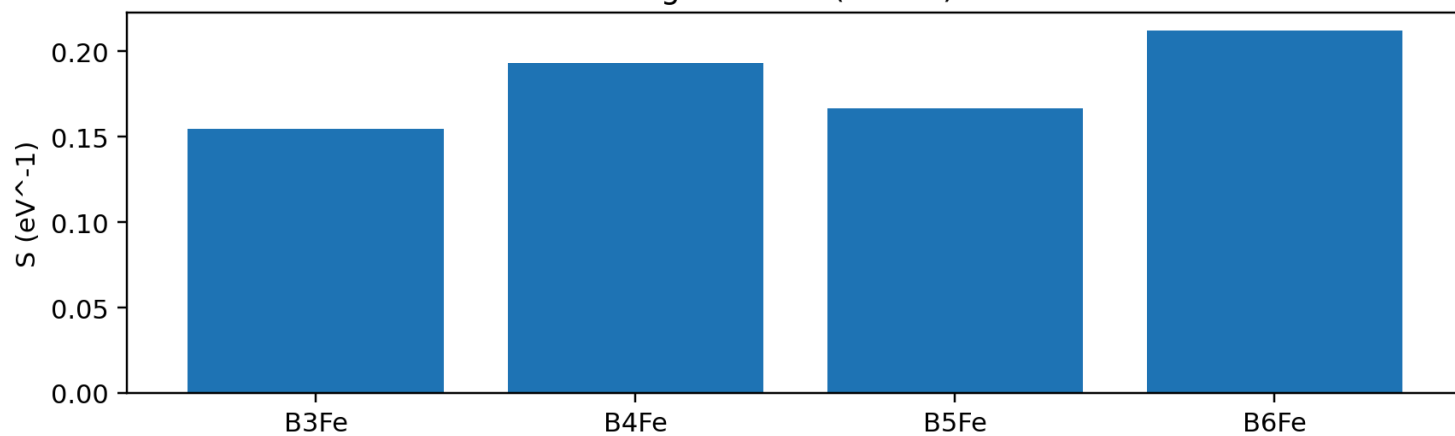


Figure 4C. ω (eV)

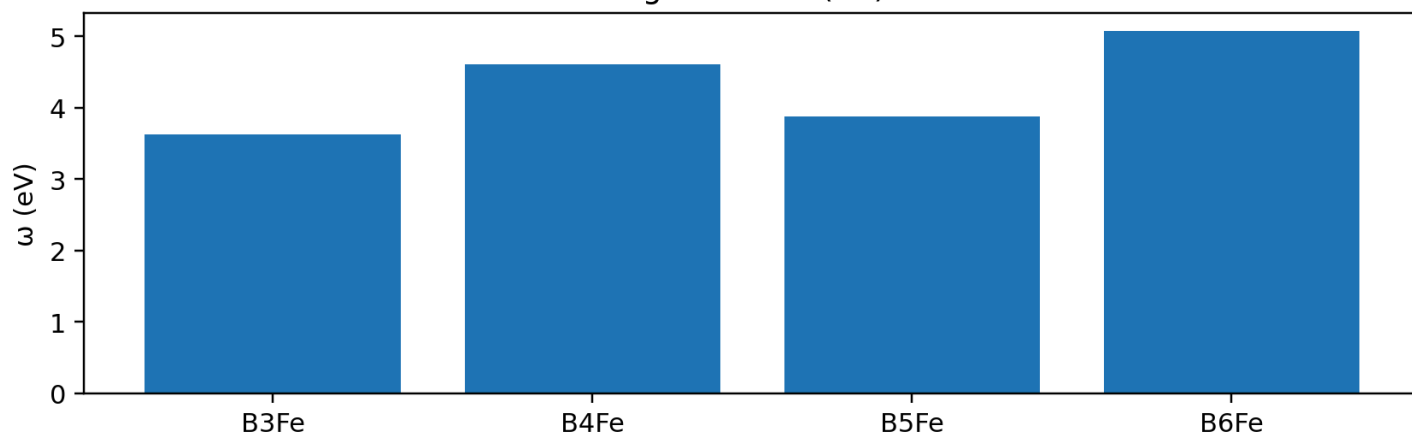


Figure 4

Comparative global reactivity profile of B3Fe-B6Fe based on the conceptual-DFT descriptors η , S , and ω .

Figure 6. Optimized H₂-bound structures of B_nFe-H₂ complexes from uploaded outputs

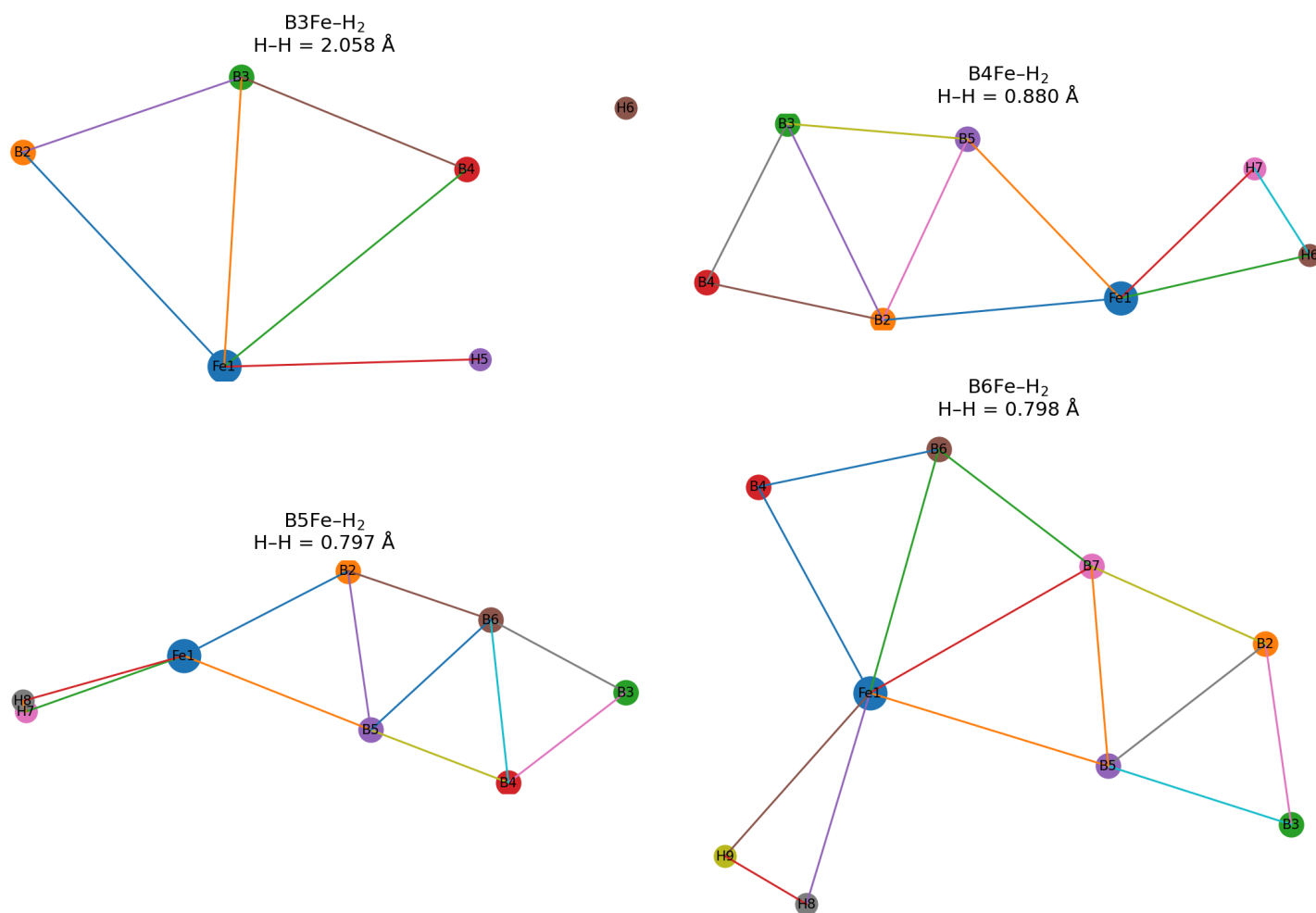


Figure 5

See image above for figure legend

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [coordinates.zip](#)
- [outputs.zip](#)
- [BnFeJMMNumericalData.xlsx](#)
- [BnFeJMMSupplementaryInformation.pdf](#)