Electronic Supplementary Information (ESI)

2Ch-2N square and hexagon interactions: a combined crystallographic data analysis and computational study

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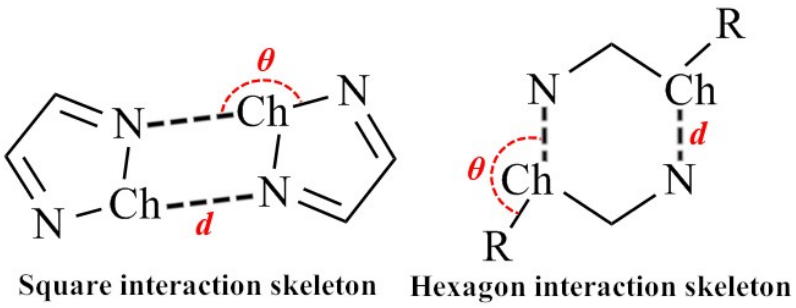

Fig. S1 The skeletons used in the CSD survey. For the skeleton of hexagon interactions, the R, Ch, C and N atoms are all in the rings.

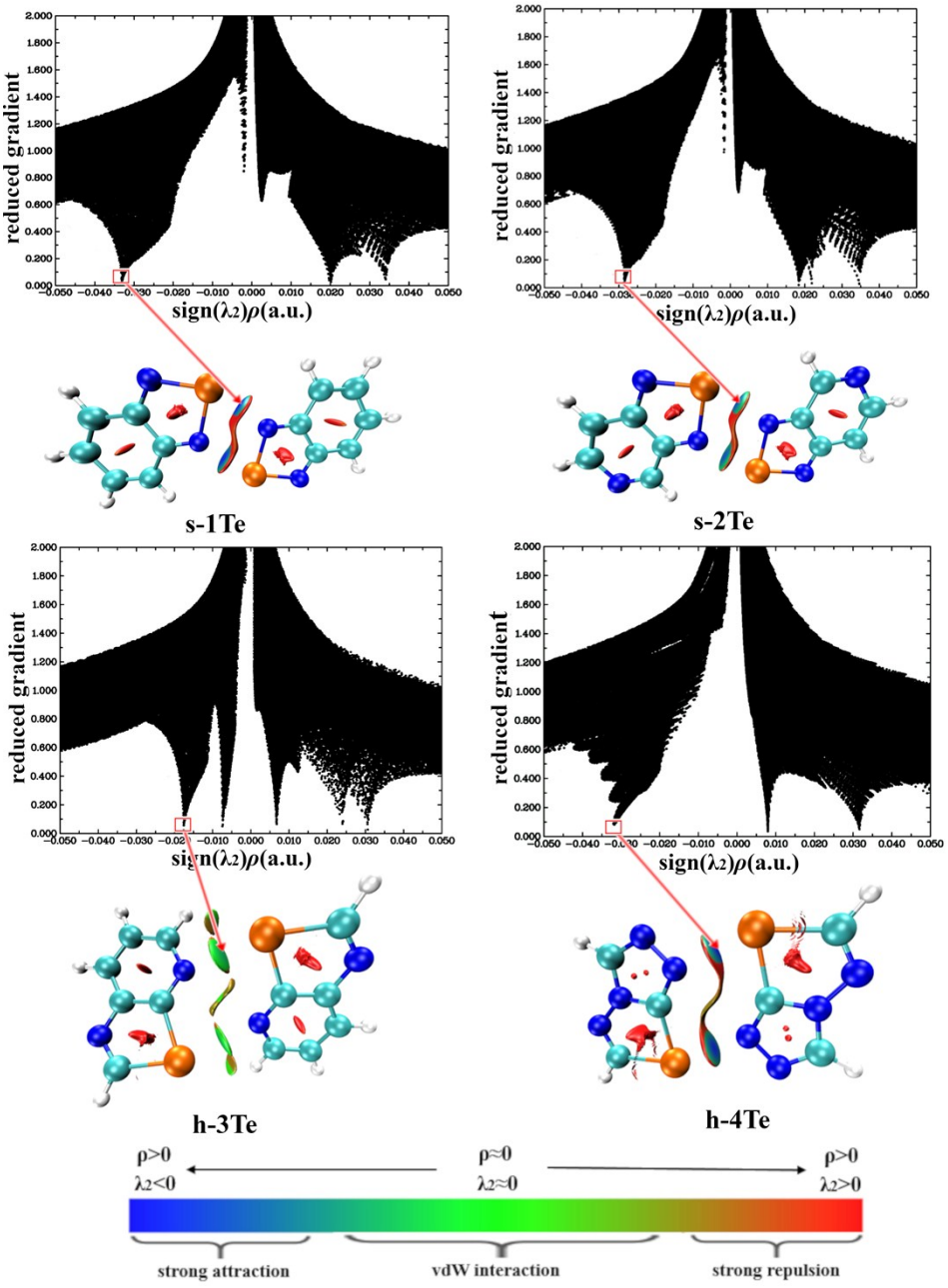

Fig. S2 NCI isosurfaces and plots of s versus ρ multiplied by the sign of λ_2 for the four selected dimers.

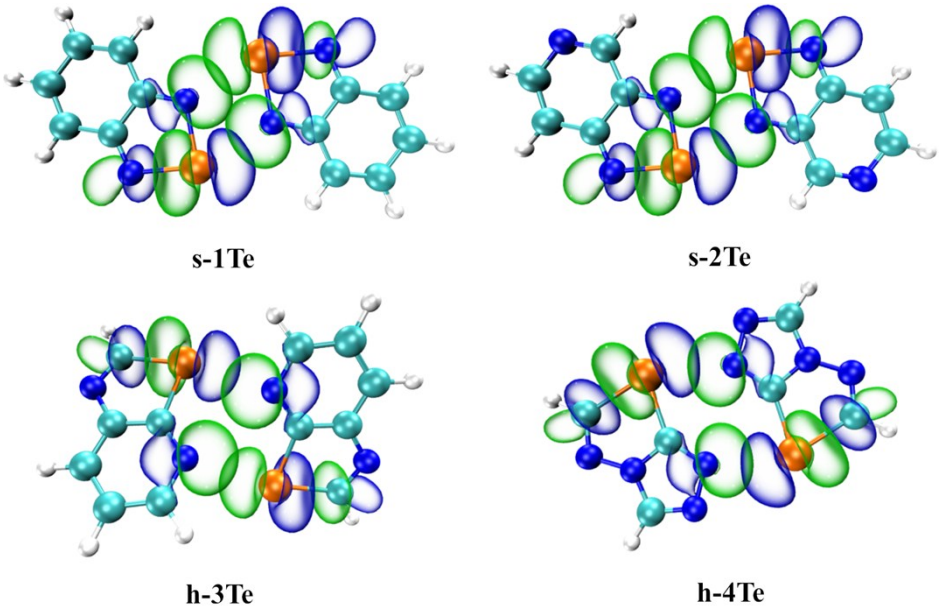

Fig. S3 NBO plots for the four selected dimers.

Table S1. The NBO values of $E^{(2)}$ (kcal/mol) for the four selected dimers[a]

Dimers	donor	acceptor	$E^{(2)}$
s-1Te	LP(N)	BD*(N−Te)	14.98
s-2Te	LP(N)	BD*(N−Te)	12.19
h-3Te	LP(N)	BD*(C−Te)	5.17
h-4Te	LP(N)	BD*(C−Te)	14.18

[a]LP represents the lone pair orbital, and BD* denotes the anti-bonding orbital.

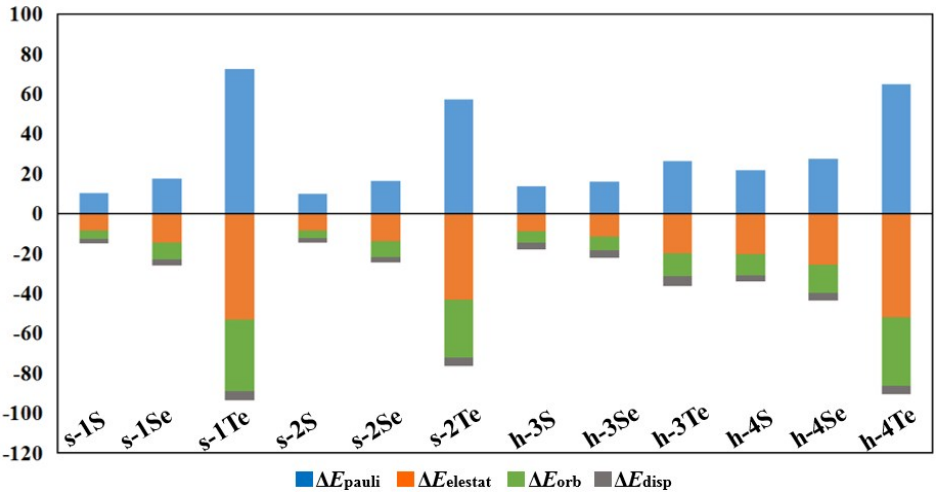

Fig. S4 The four components of the binding energies obtained by the EDA scheme for the twelve dimers. The scales are given in kcal/mol.

Table S2. EDA results for the dimers under study[a]

Dimers	ΔE_{Total}	ΔE_{Pauli}	$\Delta E_{elestat}$	ΔE_{orb}	ΔE_{disp}
			The dimers of 1 and 2		
s-1S	-4.61	10.22	-8.58 (57.9%)	-3.93 (26.5%)	-2.32 (15.6%)
s-1Se	-8.38	17.50	-14.65 (56.6%)	-8.24 (31.8%)	-2.99 (11.6%)
s-1Te	-21.21	72.30	-53.03 (56.7%)	-36.04 (38.5%)	-4.44 (4.7%)
s-2S	-4.81	9.73	-8.49 (58.4%)	-3.77 (25.9%)	-2.28 (15.7%)
s-2Se	-8.31	16.24	-13.90 (56.6%)	-7.73 (31.5%)	-2.92 (11.9%)
s-2Te	-19.27	57.13	-43.05 (56.3%)	-29.04 (38.0%)	-4.31 (5.6%)
			The dimers of 3 and 4		
h-3S	-4.48	13.58	-8.96 (49.6%)	-5.56 (30.8%)	-3.54 (19.6%)
h-3Se	-6.21	15.94	-11.38 (51.4%)	-6.86 (31.0%)	-3.91 (17.7%)
h-3Te	-9.82	26.43	-19.78 (54.6%)	-11.54 (31.8%)	-4.93 (13.6%)
h-4S	-12.11	21.83	-20.15 (59.4%)	-10.62 (31.3%)	-3.17 (9.3%)
h-4Se	-16.08	27.27	-25.45 (58.7%)	-14.34 (33.1%)	-3.56 (8.2%)
h-4Te	-25.52	64.98	-51.96 (57.4%)	-34.16 (37.7%)	-4.38 (4.8%)

[a]All values are given in kcal/mol.

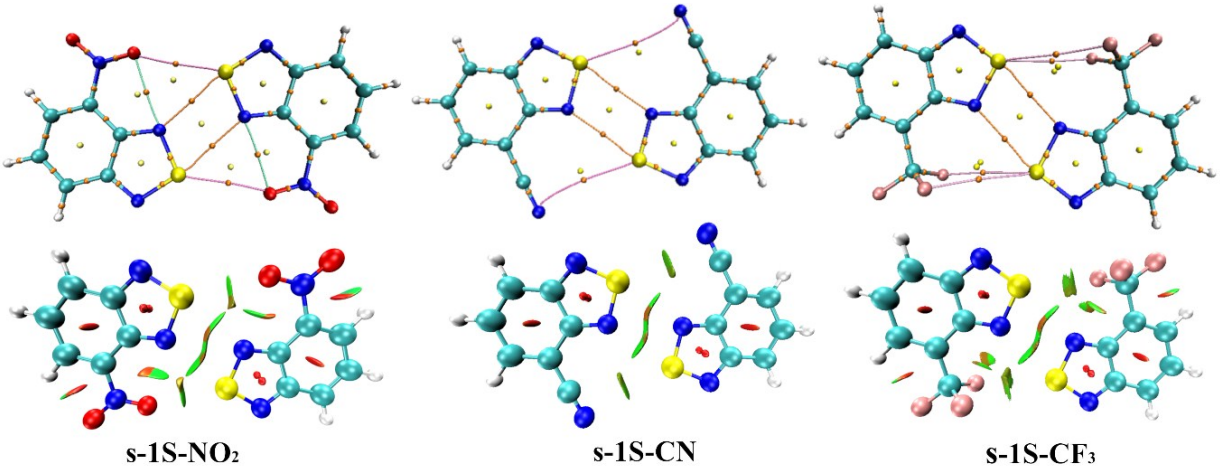

Fig. S5 The AIM graphs (above) and NCI isosurfaces (below) for the three selected dimers.

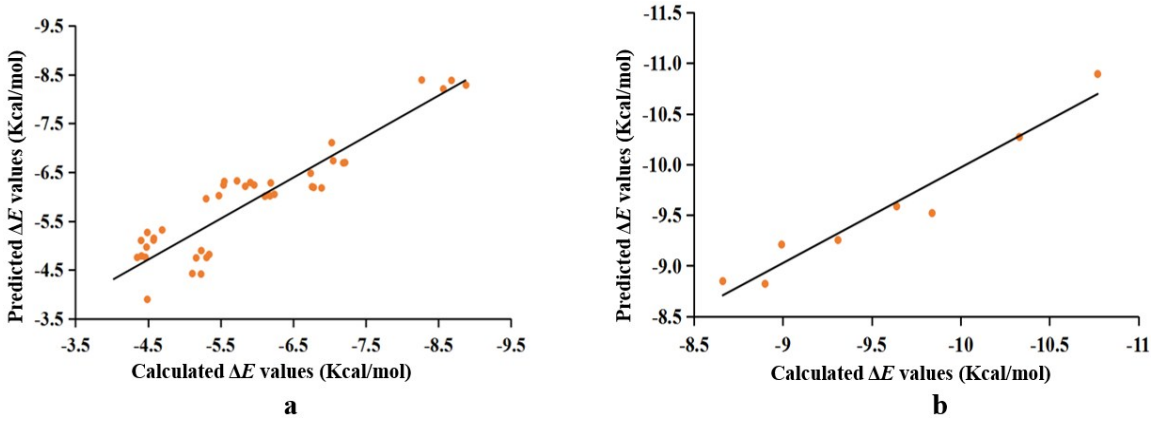

Fig. S6 Plots of the binding energies calculated with the M06-2x-D3 method versus those predicted by Equation 1 (a) and Equation 2 (b).

The results of the CSD search

(1) The crystal structures containing 2Ch-2N square interaction motifs

a. The skeleton of the dimer of 1

ACEDEU	ELITAW	IFOGAM	NABSIV	SAXPOW07
ACIQUB	ESUYEW	IJAZOK	NABSOB	SAYKIN
AMBRCD	EXADUE	IJOBOZ	NABSUH	SAYKOT
ANQSDZ	FEBYAO	IJOVEK	NANPAW	SIDKEY
ANQTDZ	FELPUH	IMUTEQ	NANPEA	SIWMAO
AREGOU	FEYMUT	IMUTEQ01	NANQUR	TUFJUA
AROPII	FIJSAV	IMUTOA	NAVPOS	UJIWEQ01
ASIQAU	FITKOK	JIBWAV	NEVXOB	ULUJES
BEVPEZ	FITKUQ	JIBWEZ	NONZIZ	UQISOE
BEVPID	FITLAX	JIBWOJ	NUDCAR	USALOR
BEVPOJ	FODKOA	JIBWUP	NUFDAT	USALUX
BEVPUP	FODKOA01	JIWTUH	NUTCIQ	USAMAE
BEVQAW	FODLIV	JIWVAP	NUTCOW	USAMEI
BEVQEA	FODMAO	JIWVIX	NUTDAJ	USANOT
BIGLIO	FODMAO01	JIWWEU	OGUYUK	USANUZ
BURTIT	FOZTAR	JIWWOE	ONINIJ	USAPAH
BURTIT01	FOZTAR01	JIXFEE	OVIWOH	USAPEL
CANQTZ	FOZTEV	JIXFOO	OVIXIC	UYIVAB
CEDXOB	FOZTIZ	JIXFUU	OXAZIY	UYUSEO
CEZFUL	GAJQIU	JOTPAL	OXAZOE	UZANAM
CIGYAV	GAJQUG	JUQTEW	PATWOZ	UZAQAP
COFMUF10	GAJRAN	JURLAJ	PEZBAZ	UZEMOD
COGTIB	GAJRER	KAZNOQ	PIFNIC	UZEMUJ
COWNEJ01	GAJRIV	KESREI	POFGIB	VAMMIH
COWNOT	GAJROB	KESROS	QARSEI01	VEHVIQ

DAVRAW	GAJRUH	KIBVEY	QIBREB	VEHVUC
DAVRIE	GAJSAO	KIGHUG	QIBROL	VEKYOA
DAVSEB	GAJSAO01	KODXEI	QIJWOY	WEBLUM
DEBHEY	GAJSIW	KODXIM	QOGPIL	WESYAX
DEBHIC	GAJSOC	KODXOS	QOKVUJ	XADWAD
DEBHOI	GASDUC	LEKLAR	QUGDIH	XIDGOI
DEXTEI	GASFAK	LISYIY	RAGXEF	YAKZAO
DIVSOT	GASFEO	LISYOE	REVYAT	YEVWAA
DIVSUZ	GINTII	MELCAK	RUPPEY	YEVWII
DIVTAG	GIRFAQ	MELCEO	RUTYUC	YIWLOG
DIVTEK	HARCIO	MOPHOO	SAXPOW	YULXIN
DIVTUA	HARCOU	NABRAM	SAXPOW01	ZIJRIV
DIVZUG	HIWHAY	NABREQ	SAXPOW02	ZIJROB
DIWPAP	HUDHUL	NABROA	SAXPOW03	ZUCDIM
DORZOA	HULHIF	NABRUG	SAXPOW04	ZUCLEQ
EGOQAU	HULHIF01	NABSAN	SAXPOW05	ZUFKIW
EJIYED	HUYMUL	NABSER	SAXPOW06	

b. The skeleton of the dimer of 2

BAYNEX	GIPDER	UXINIZ	WEJYER	WEJZAO
CEWWOS	GIPDIV	ROJSAK	WEJYIV	
CEWXAF	LIZPAM	ROJSEO	WEJYOB	
GIPDAN	POMVEU	WEJXUG	WEJYUH	

c. Other skeletons

AHIKEJ	CEJPAI	IVECAN	NEXPEL	TABXEZ
AREGEK	DPSEAZ	KANVAX	NIGLUM	TEGMOJ
AREGEK01	EFIWOG	KOZJEO	PIVWUM01	TEGNAW
BAPREQ	EKEKOU	KOZJIS	POYKOD	TEGNEA
BIBCUL	GUKWUE	LAMLOC	RIJNAB	WEJXEQ
BIMLAK	HAMFOS	MUDCAQ	SOTQUP	

(2) The crystal structures containing 2Ch-2N hexagon interaction motifs

a. The skeleton of the dimer of 3

AKOQEY	BEYGEU	BEYHAR	BEYJAT	KAWCAP
BEYFOD	BEYHOF	BEYGUK	BEYGOE	PIHJAT
BEYGAQ	BEYHIZ	BEYHEV	BEYJEX	

b. The skeleton of the dimer of 4

CINRAV	GIGRAQ	MPTZTD	URAQIO	YAXSUN
CINREZ	GUVHOV	OWEDEA	UXIPOI	YESBAA
CICNOS	HODNOE	SAPRAD	VAHGUH	YIRHEN
GAJCOM	HOWMUD	TELLEB	WAWPIU	
GAJDAZ	KAZQUZ	TOMRAQ	WUDXID	
GAJDED	MODTUV	ULAREG	XERZUQ	

c. Other skeletons

NIPYUJ	FEFCID	NEWYIX	SAXPOW06	WAGJOF01
AHOVID	FILHOA	OHALAM	SAXPOW07	WAGJOF02
AHOVID01	FINLEU	PAWCIB	SOLRUI	WEVZEC
BAHBOD	FUCMUL	PENXIQ	TAXZEZ	WIPJOW
BEZQAZ	HAJZUQ	QONJAF	TEYZUS	XARHII01
BEZQAZ01	HEMXEC	QUDSOX	TICNEY	XINCEC
BEZQAZ02	HULGOK	SAXPOW	TUFCAY	XINCEC01
BEZQAZ03	IMTZBI	SAXPOW01	TUGGIL	XOQHER
COSLOL	MBTHFX	SAXPOW02	TUGGIL01	XURJUP
DILCUY	METROT	SAXPOW03	TZBZTZ	YOBZOG
FAMWUL	NEWYET	SAXPOW04	VACMAN	ZAPRAM
FAMXAS	NEWYET01	SAXPOW05	WAGJOF	ZOPGOA