Supporting information

Binding Energy in Cluster (BEC): An Effective Bridge Connecting Microscopic Structure and Macroscopic Properties of Molecular Crystal Materials

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1. The calculation details for E_{lat} and E_{avg} of four compounds with structurally similar and isomers

We calculated the lattice energies (E_{lat}) of the four energetic compounds prepared here using the PBE/DZVP[1,2] theory with the DFT-D3(BJ)[3,4] dispersion correction in the software package CP2K[5,6] and Multiwfn program[7] (Table S1).

Table S1. T_m, E_{avg}, and E_{lat} of four compounds.

Compound	1,1,2,2-CNE	1,1,3,3-CNE	ETN	MHN
T_m (°C)	85.9	146.9	62.5	110.7
E_{lat} (kJ mol^{-1})	-110.04	-98.03	-66.85	-59.14
E_{avg} (kJ mol^{-1})	-23.12	23.57	-20.51	-21.22

We extracted a molecular cluster that consisted of the central molecule (i.e., the one closest to the geometric centre of the supercell) and adjacent molecules (with the shortest interatomic distances between the central and adjacent molecules of less than 1.2 times the sum of van der Waals radius regarding with the closest atoms) by extending the unit cell in certain multiples. For example, fourteen dimers were identified in the crystal structure of 1,1,2,2-CNE, and all dimers formed a molecular cluster (Fig. S1a). Then, we used the symmetry-adapted perturbation theory (SAPT) method to calculate the weak interactions energies between these fourteen dimers implemented in the PSI4 package at the theory level of sSAPT0/jun-cc-pVDZ theory, see Table S2-S5 for detailed data of four compounds. In Fig. S1, it can be observed that the distribution of dimer binding energies for the four compounds.

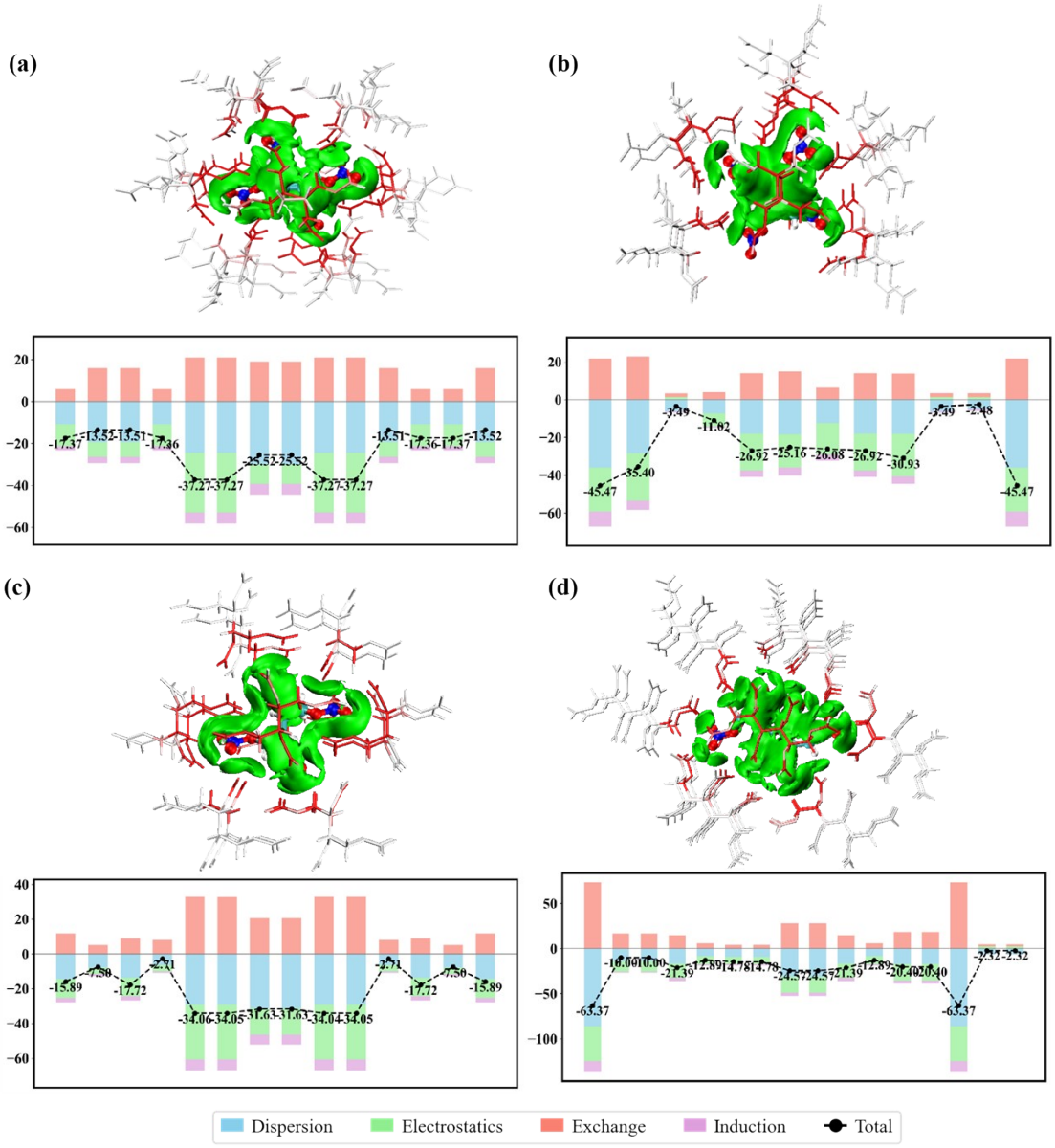

Figure S1 Molecular cluster, weak intermolecular interaction energies (kJ mol^{-1}) and energy decomposition of the dimers in compounds. (a), (b), (c), and (d) are 1,1,2,2-CNE, 1,1,3,3-CNE, ETN, and MHN, respectively.

Table S2. The total binding energies (kJ mol^{-1}) and energy decomposition of the different dimers of compound 1,1,2,2-CNE.

	Dispersion	Electrostatics	Exchange	Induction	tot
1	-10.81095997	-10.48405366	5.90711356	-1.97784271	-17.36574278
2	-19.28398427	-7.04008966	15.86870924	-3.06286357	-13.51822826
3	-19.28327839	-7.03355243	15.86661997	-3.06264053	-13.51285138
4	-10.81118314	-10.48312344	5.90740836	-1.9774642	-17.36436242
5	-24.5416226	-28.34804053	21.00091624	-5.37778397	-37.26653086
6	-24.54187622	-28.34990736	21.00178884	-5.37791763	-37.26791237
7	-30.02210806	-9.31674115	18.97450156	-5.15871188	-25.52305953
8	-30.02210719	-9.31673357	18.97450153	-5.15869808	-25.52303731

9	-24.54162255	-28.34800509	21.00091623	-5.37777718	-37.26648859
10	-24.5418762	-28.34988405	21.00178884	-5.37791881	-37.26789022
11	-19.28327847	-7.03356904	15.86661994	-3.06265229	-13.51287986
12	-10.81118305	-10.48309746	5.90740837	-1.97746041	-17.36433255
13	-10.81096005	-10.48410621	5.90711357	-1.97784838	-17.36580107
14	-19.28398424	-7.04007839	15.86870926	-3.06286379	-13.51821716

Table S3. The total binding energies (kJ mol^{-1}) and energy decomposition of the different dimers of compound 1,1,3,3-CNE.

	Dispersion	Electrostatics	Exchange	Induction	tot
1	-36.02318232	-23.17168204	21.83121436	-8.10386519	-45.46751519
2	-28.30654744	-25.32979336	22.92230361	-4.68898044	-35.40301763
3	-6.16513343	1.28369595	2.10851431	-0.71829868	-3.49122185
4	-7.37327225	-6.69815952	3.93088345	-0.87615566	-11.01670398
5	-17.95684311	-19.55333633	14.11420616	-3.52703835	-26.92301163
6	-18.26431486	-17.66839799	15.03535947	-4.26553969	-25.16289307
7	-12.48698331	-16.60655383	6.27766291	-3.26318473	-26.07905896
8	-17.95694774	-19.55474055	14.11426005	-3.52721101	-26.92463925
9	-18.02228002	-22.49297932	13.69976021	-4.11489779	-30.93039692
10	-6.16520334	1.28403869	2.10852951	-0.71829625	-3.49093139
11	-5.18041314	1.22579971	2.21792607	-0.73917311	-2.47586047
12	-36.02318211	-23.17170785	21.83121436	-8.10386731	-45.46754291

Table S4. The total binding energies (kJ mol^{-1}) and energy decomposition of the different dimers of compound ETN.

	Dispersion	Electrostatics	Exchange	Induction	tot
1	-14.30248924	-11.08345086	11.81213103	-2.31648005	-15.89028912
2	-7.99754642	-3.65546131	5.15445271	-1.00501898	-7.503574
3	-13.66730762	-10.59889002	9.03741475	-2.48692149	-17.71570438
4	-6.44527178	-3.47950091	8.10688685	-0.89667648	-2.71456232
5	-29.2505924	-31.40867063	32.72034175	-6.11745742	-34.0563787
6	-29.24778948	-31.39359781	32.71060682	-6.11559473	-34.0463752
7	-31.23243164	-15.11992089	20.55700531	-5.83519091	-31.63053813
8	-31.23243169	-15.11988328	20.55700534	-5.83519392	-31.63050355
9	-29.25032142	-31.39663861	32.71804682	-6.11591494	-34.04482815
10	-29.2511659	-31.40337829	32.72032688	-6.11647554	-34.05069285
11	-6.44514057	-3.47942877	8.10686727	-0.89663934	-2.71434141
12	-13.66773014	-10.60228561	9.03857355	-2.48712864	-17.71857084
13	-7.99726219	-3.65522528	5.15374706	-1.00489428	-7.50363469
14	-14.30276819	-11.08118345	11.81257694	-2.31628017	-15.88765487

Table S5. The total binding energies (kJ mol^{-1}) and energy decomposition of the different dimers of compound MHN.

	Dispersion	Electrostatics	Exchange	Induction	tot
1	-86.03223745	-38.77386603	73.7222581	-12.29063468	-63.37448006

2	-14.1462111	-11.39511638	16.89208426	-1.34863239	-9.99787561
3	-14.14714417	-11.39752534	16.8940593	-1.34881485	-9.99942506
4	-16.49851156	-16.18827998	14.7784827	-3.4865131	-21.39482194
5	-8.2500007	-9.53413772	6.00986733	-1.11227	-12.88654109
6	-9.25707404	-7.99512089	4.11442707	-1.63743209	-14.77519995
7	-9.25707405	-7.99521037	4.11442706	-1.63743191	-14.77528927
8	-30.93240426	-18.32165133	28.02077889	-3.34146568	-24.57474238
9	-30.93342752	-18.32021162	28.02327758	-3.34171496	-24.57207652
10	-16.49894906	-16.1875947	14.77976357	-3.48668064	-21.39346083
11	-8.24999613	-9.53469328	6.00989354	-1.11239077	-12.88718664
12	-16.94642736	-18.61274402	18.39061539	-3.23287782	-20.40143381
13	-16.94642753	-18.61288299	18.39061535	-3.23288487	-20.40158004
14	-86.03223881	-38.77379162	73.722258	-12.29067078	-63.37444321
15	-6.28246159	2.27311236	2.13178691	-0.44499276	-2.32255508
16	-6.28240017	2.27468762	2.13176342	-0.44514138	-2.32109051

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