Supporting Information

Diiodomethane as Halogen Bond Donor toward Metal-bound Halides

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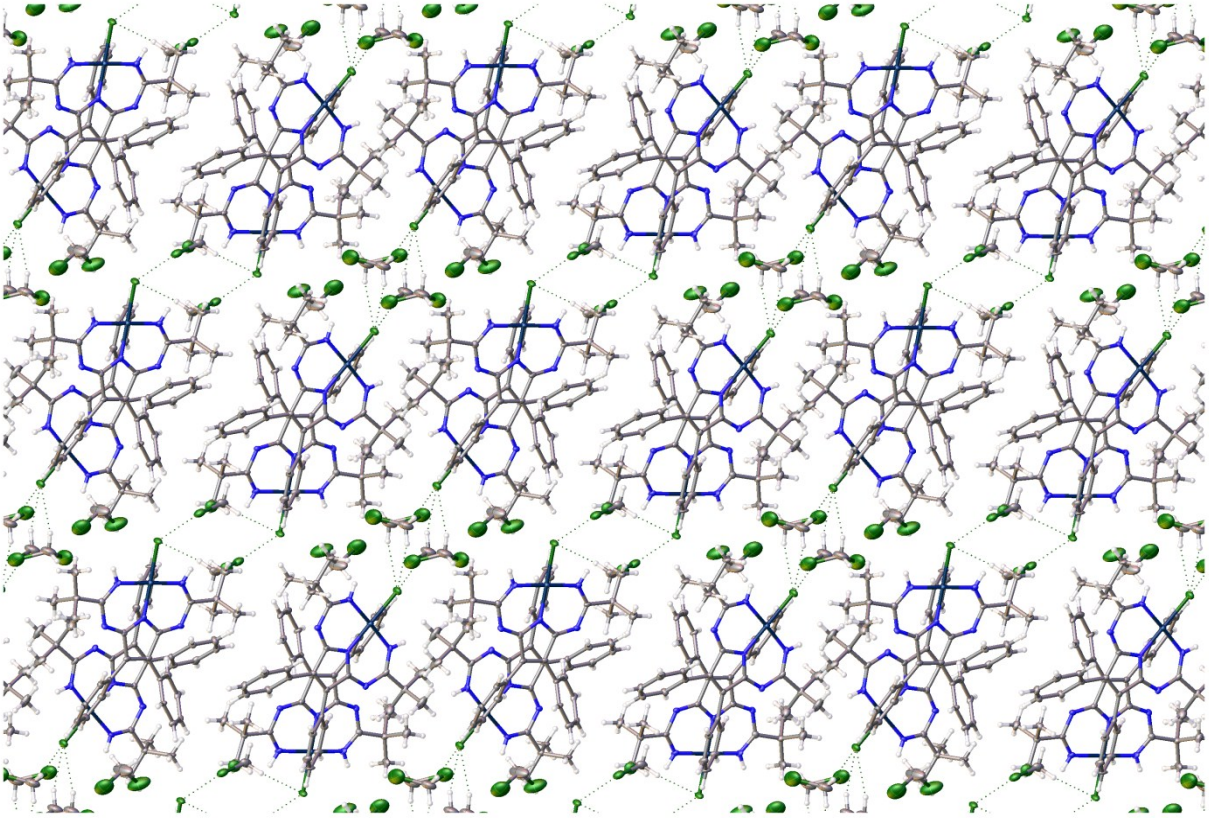
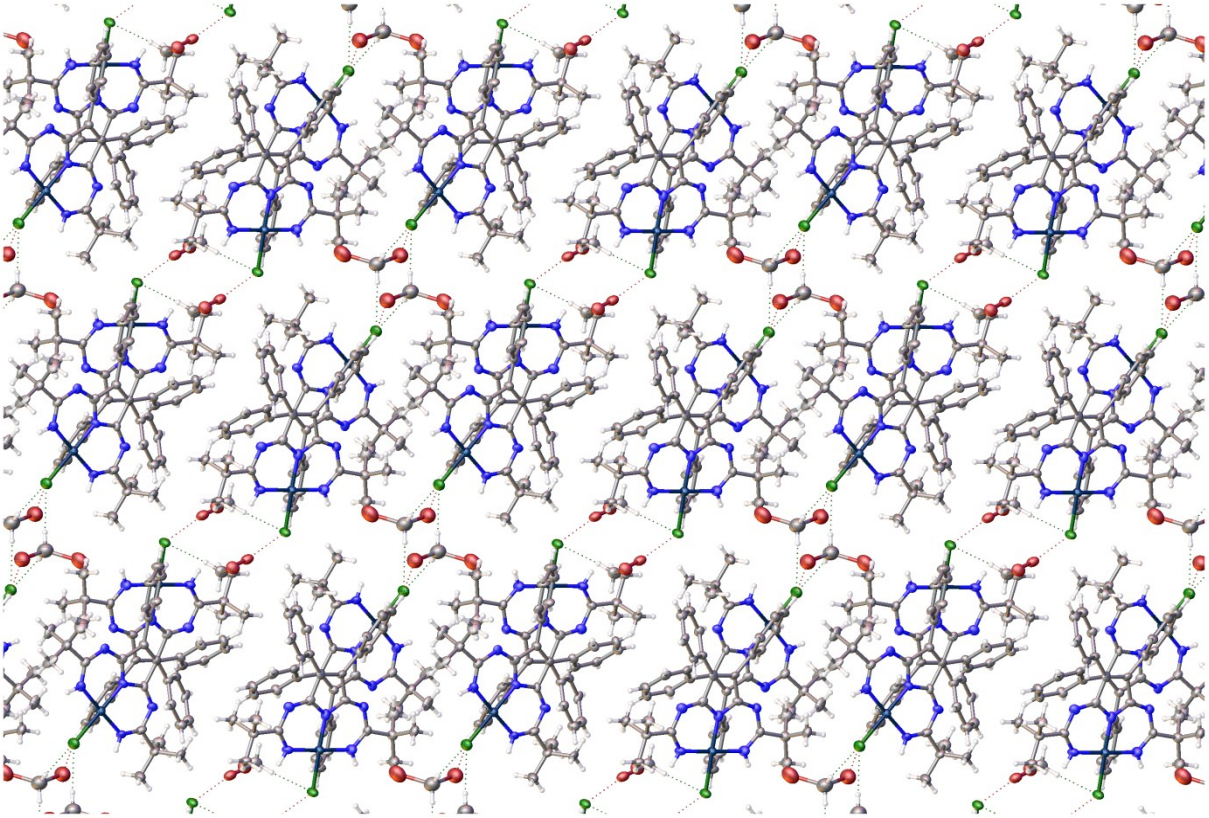


a



b

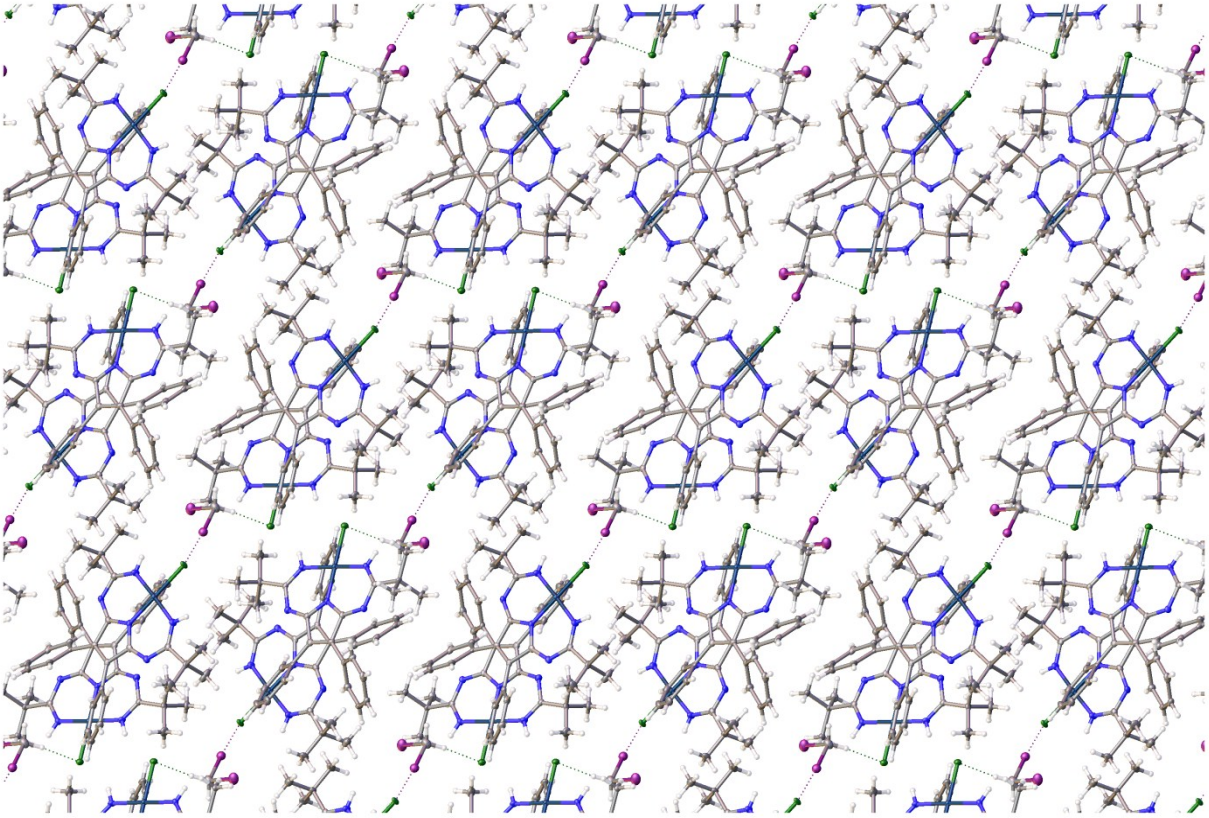


Figure S1. Packing of (***a***), (***b***), and (***c***), views along *a* axis.

It is indicated in the main text that previously we reported the structures of solvates **1**•1¼CH_2Cl_2 and **1**•1⅖CH_2Br_2, which demonstrate the same packing features (**Figure S1**, ***a*** and ***b***) being the successful examples of the Cl/Br isostructural exchange. Although the solvate **1**•½CH_2I_2 is not the same, it resembles the previous two in its packing mode (**Figure S1**, ***c***). All these structures exhibit the layered motif, where the layers form complex molecules alternate with the voids filled by solvent.

Table S1. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$, energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (Hartree) at the bond critical points (3, –1), corresponding to the intermolecular intermolecular I•••I XBs in solid state structure of $(\mathbf{2})_2$•(CH_2I_2), bond lengths – *l* (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by two approaches.

Contact	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}[a]	E_{int}[b]	*l*
I•••I	0.012	0.038	0.001	-0.008	0.009	2.5	2.4	3.65
I•••I	0.013	0.041	0.001	-0.009	0.010	2.8	2.7	3.59

[a] $E_{int} = -V(\mathbf{r})/2$ [1]
[b] $E_{int} = 0.429G(\mathbf{r})$ [2]

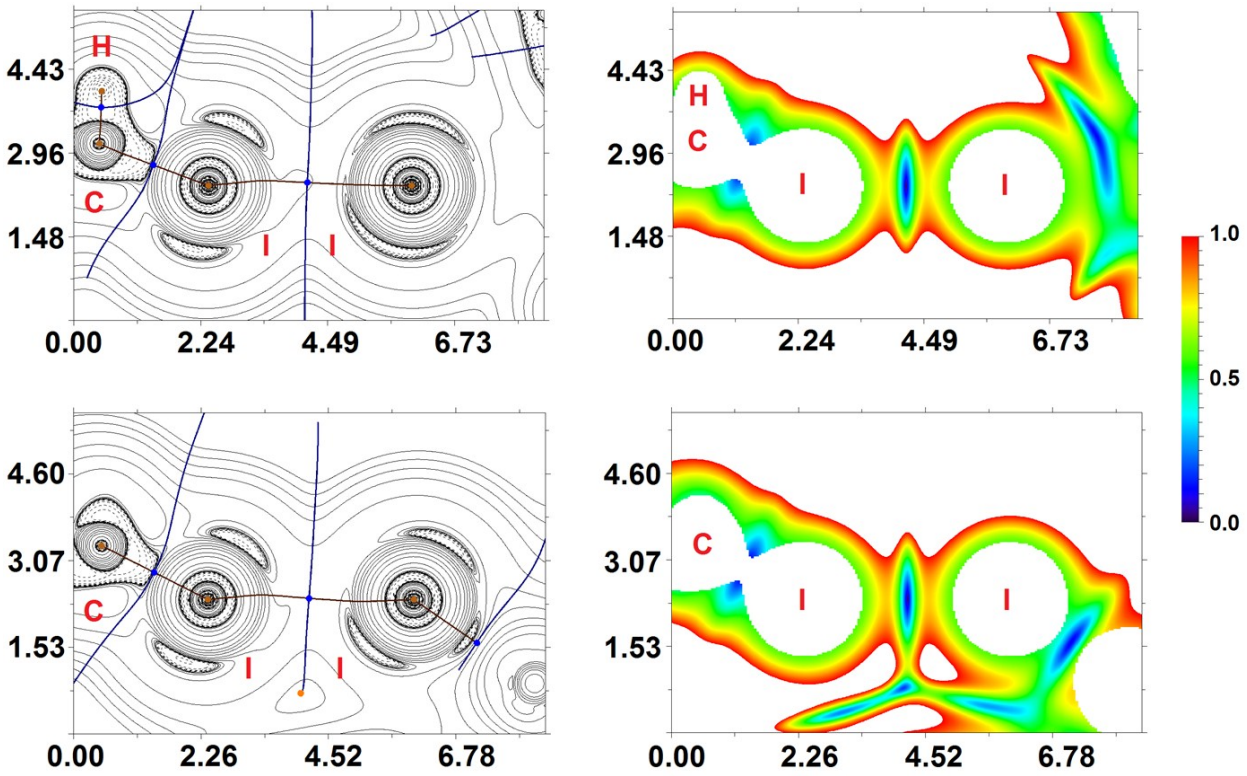


Figure S2. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$, bond paths and selected zero-flux surfaces (left) and RDG isosurfaces referring to the non-covalent interactions (right) for intermolecular I•••I XBs in cluster $(\mathbf{2})_2$•(CH_2I_2) from VEMWOA. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown. Length units – Å, RDG isosurface values are given in Hartree.

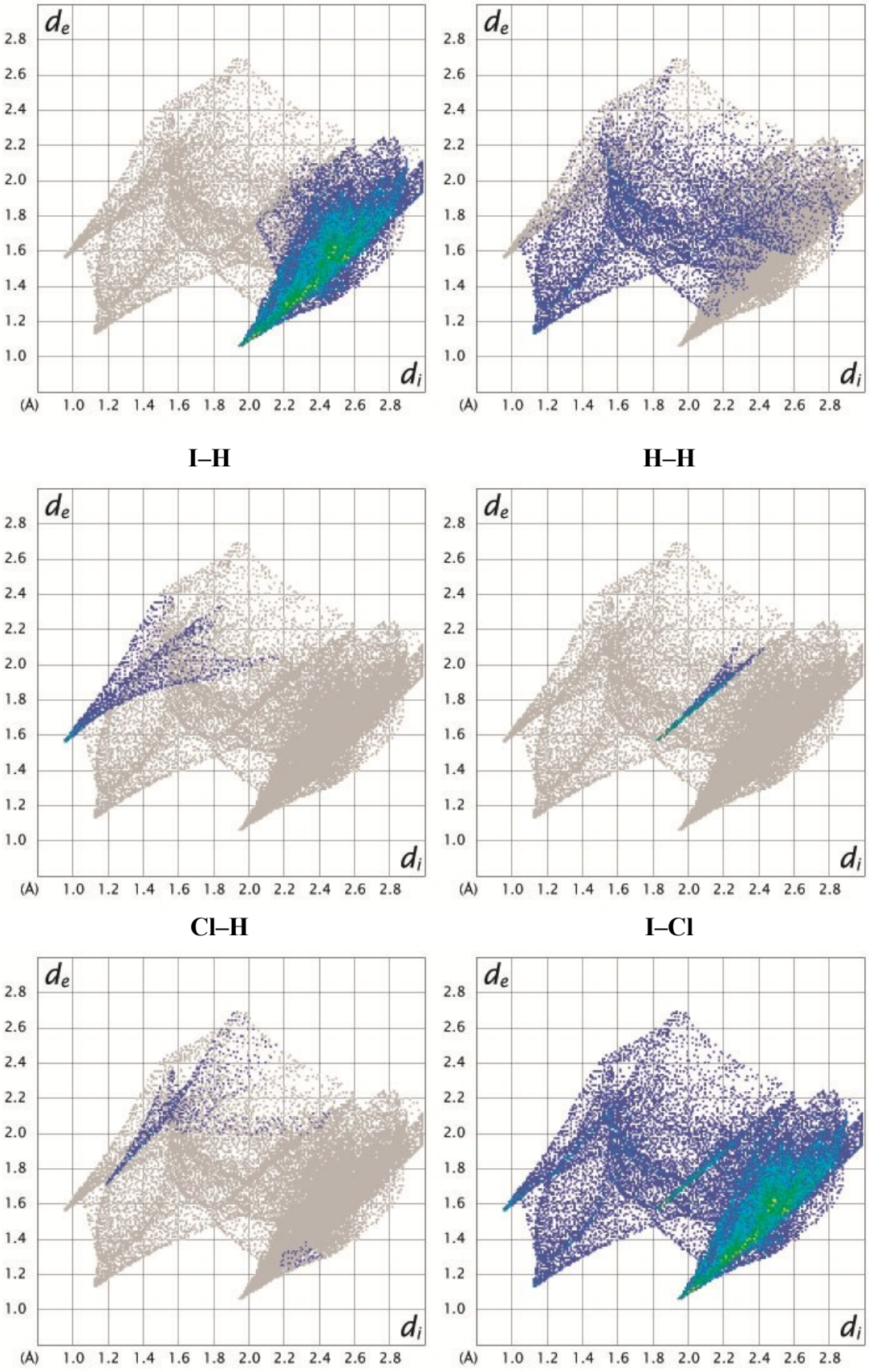


Figure S3. The Hirshfeld surface fingerprint plots for CH_2I_2 in $(\mathbf{1})_2$•(CH_2I_2).

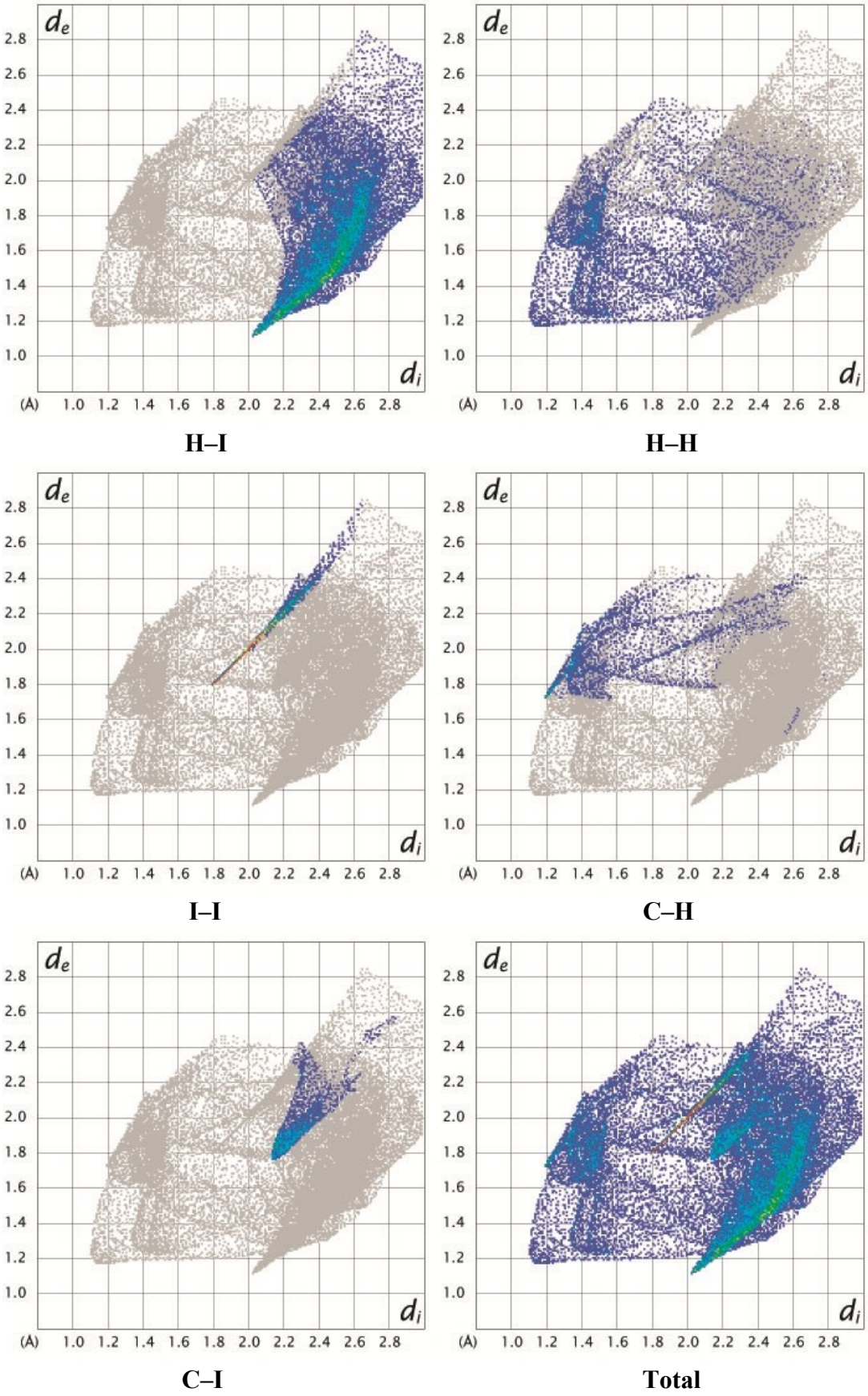


Figure S4. The Hirshfeld surface fingerprint plots for CH_2I_2 in solvate VEMWOA.

Table S2. Crystal data and structure refinement for **1**•½CH_2I_2.

Identification code	**1**•½CH_2I_2
Empirical formula	$C_{53}H_{62}N_{10}Cl_2I_2Pt_2$
Formula weight	1554.00
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.8895(2)
b/Å	15.6795(4)
c/Å	16.3632(3)
α/°	99.4445(18)
β/°	93.0501(15)
γ/°	93.7936(17)
V/Å^3	2744.15(10)
Z	2
ρ_{calc}g/cm^3	1.881
μ/mm^{-1}	6.360
F(000)	1492.0
Crystal size/mm^3	0.16 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range/°	6.088 to 52.998
Index ranges	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	50780
Independent reflections	11374 [R_{int} = 0.0602, R_{sigma} = 0.0479]
Data/restraints/parameters	11374/0/634
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0289, wR_2 = 0.0625
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0673
Largest diff. peak/hole / e Å^{-3}	1.18/-1.04

Table S3. The Cartesian atomic coordinates of the (**1**)$_2$•(CH_2I_2) model cluster.

Atom	X	Y	Z
Pt	10.421443	6.489818	4.227004
Cl	11.051766	8.736281	4.366492
N	11.531644	6.053446	5.792138
H	11.959691	6.712461	6.138442
N	9.930323	4.610037	4.083167
N	9.276165	6.852112	2.670569
H	9.231911	7.675600	2.428961

N	8.482014	4.683216	2.159971
N	11.174181	3.720584	5.930660
C	8.573631	6.020625	1.950578
C	11.708446	4.897896	6.375217
C	9.099636	4.074627	3.140898
C	10.397644	3.614973	4.890136
C	9.012621	2.613283	3.388948
C	6.872213	1.919288	2.303325
H	6.494321	2.734122	2.543322
C	11.383958	0.737251	5.581134
H	12.071685	1.353776	5.479659
C	8.773020	0.466660	2.151918
H	9.673505	0.295787	2.309768
C	8.219018	1.669173	2.577147
C	9.330208	-1.083384	5.945156
H	8.640078	-1.690122	6.090121
C	10.091503	1.044832	5.117248
C	8.005763	-0.475211	1.501188
H	8.396799	-1.262115	1.198373
C	9.816189	2.318674	4.455243
C	7.797403	6.513063	0.715158
C	9.066793	0.115381	5.310534
H	8.205982	0.302345	5.012551
C	6.648526	-0.250996	1.296627
H	6.115247	-0.907558	0.908444
C	12.506317	4.788996	7.673455
C	6.101005	0.963907	1.676756
H	5.202307	1.136979	1.506020
C	7.613290	8.041594	0.715158

H	7.146151	8.307888	1.510852
H	7.105176	8.303111	-0.056375
H	8.472991	8.468136	0.690998
C	11.633763	-0.475616	6.188374
H	12.493973	-0.678415	6.478303
C	8.597522	6.099563	-0.510597
H	9.474948	6.486124	-0.465497
H	8.152869	6.410024	-1.303070
H	8.670512	5.142334	-0.539590
C	11.492926	4.944099	8.809011
H	11.120031	5.829044	8.784850
H	11.930676	4.803471	9.651416
H	10.790281	4.299161	8.701093
C	10.616559	-1.392192	6.370385
H	10.792581	-2.210312	6.773064
C	6.409581	5.861570	0.700662
H	6.503581	4.906900	0.647508
H	5.915826	6.176196	-0.061207
H	5.938844	6.092071	1.504410
C	13.584951	5.868044	7.786205
H	14.198067	5.786869	7.051718
H	14.060716	5.759616	8.614114
H	13.173908	6.735504	7.763655
C	13.176747	3.423533	7.781373
H	12.508542	2.736035	7.739495
H	13.646770	3.362505	8.615725
H	13.795651	3.312822	7.054940
I	8.269234	10.679753	4.068349
I	4.953991	11.204693	2.828580

C	6.668636	12.060365	3.743306
H	6.407853	12.441925	4.596986
H	6.990364	12.784680	3.184387
Pt	3.989334	15.030958	5.641697
N	5.042178	16.118163	6.900311
H	5.501874	15.667004	7.472116
N	3.350163	16.685900	4.838593
N	2.851428	14.017056	4.397257
H	2.890461	13.159849	4.469739
C	2.048299	14.470990	3.479148
N	1.910635	15.789796	3.131234
N	4.598867	18.300714	6.120724
C	3.805146	17.932496	5.143019
C	5.152285	17.392586	7.005008
C	2.515385	16.749785	3.767467
C	1.617744	18.603081	2.176079
C	3.472414	20.343807	4.205582
C	1.189199	13.531363	2.631911
C	2.440115	21.266599	3.968806
H	1.581948	20.960824	3.780353
C	4.760335	20.823855	4.472961
H	5.451417	20.222932	4.638865
C	3.197776	18.892932	4.181421
C	2.408219	18.181280	3.355123
C	0.091131	19.458056	0.008054
H	-0.424612	19.759468	-0.703883
C	1.403509	19.887027	0.153018
H	1.776364	20.456857	-0.481604
C	-0.216307	14.141864	2.474061

H	-0.593159	14.306887	3.340627
H	-0.779175	13.530970	1.992457
H	-0.154438	14.967744	1.989235
C	2.693224	22.624174	4.017128
H	2.005364	23.233216	3.876996
C	1.049552	12.142551	3.261702
H	1.918020	11.744593	3.356734
H	0.503482	11.587643	2.699561
H	0.638202	12.221801	4.126657
C	2.159626	19.472605	1.233809
H	3.033801	19.775274	1.330452
C	6.683684	17.012528	8.984579
H	6.056394	16.418239	9.404976
H	7.197786	17.462147	9.659469
H	7.272524	16.506670	8.419217
C	0.317617	18.149332	2.002121
H	-0.043026	17.548931	2.614193
C	5.921946	18.051737	8.138952
C	1.845029	13.429541	1.248306
H	1.966083	14.309628	0.885894
H	1.281250	12.917594	0.663615
H	2.698258	12.996508	1.328841
C	6.934006	19.053500	7.549430
H	7.620433	18.575230	7.079101
H	7.328481	19.564346	8.259756
H	6.481461	19.645255	6.942190
C	5.015236	22.181410	4.493900
H	5.877147	22.492133	4.653361
C	-0.447720	18.571957	0.937437

H	-1.320598	18.266159	0.840794
C	3.988028	23.072467	4.278064
H	4.159690	23.985889	4.307057
C	4.915074	18.794911	9.028068
H	4.449547	19.450598	8.504585
H	5.381591	19.231126	9.744837
H	4.285008	18.168276	9.390479
Cl	4.816903	13.074555	6.582195

Table S4. The Cartesian atomic coordinates of the $(\mathbf{2})_2$•(CH_2I_2) model cluster.

Atom	X	Y	Z
C	-3.768579	4.294361	18.675412
H	-3.071516	4.508936	18.020647
C	-3.204110	3.198598	19.528944
H	-3.677975	3.228639	20.373708
H	-2.282714	3.436061	19.718943
C	-3.201040	1.702295	19.061255
H	-4.095206	1.353253	19.260023
C	-3.947218	5.541757	19.508483
H	-4.616941	5.385833	20.180786
H	-4.222956	6.268451	18.944333
H	-3.115056	5.766346	19.932326
C	-2.236752	0.929825	19.949865
H	-1.341031	1.233091	19.792019
H	-2.297657	-0.007152	19.751097
H	-2.463676	1.074306	20.873551
C	-5.847870	5.401568	17.041423
C	-4.952069	6.184052	16.345735
H	-4.101794	5.852176	16.170352

C	-5.293955	7.465780	15.895584
H	-4.675648	7.996495	15.448357
C	-6.577502	7.920679	16.138198
H	-6.833123	8.757521	15.822508
C	-7.458178	7.173958	16.819270
H	-8.308514	7.507264	16.988808
C	-7.107057	5.875064	17.286960
H	-7.725182	5.357223	17.751726
C	-6.502019	3.138517	18.833257
C	-6.983283	1.862511	18.637412
H	-6.673955	1.368989	17.912494
C	-7.899664	1.301755	19.476329
H	-8.221544	0.443455	19.318484
C	-8.316201	1.986965	20.502322
H	-8.938892	1.597869	21.072318
C	-7.878220	3.255818	20.780013
H	-8.203149	3.702134	21.528315
C	-6.909493	3.909557	19.914788
H	-6.590472	4.769287	20.069710
C	-1.397752	2.273065	16.778348
C	-1.404000	3.278706	15.848815
H	-2.208164	3.524752	15.451280
C	-0.266450	3.926723	15.495126
H	-0.309210	4.609071	14.863745
C	0.913730	3.606291	16.032968
H	1.688532	4.055468	15.781585
C	0.958987	2.603510	16.959577
H	1.769881	2.371769	17.351267
C	-0.197143	1.929745	17.322036

H	-0.153372	1.237383	17.941724
C	-2.848341	-0.306127	17.117422
C	-3.933888	-1.037112	17.520804
H	-4.667275	-0.599379	17.892032
C	-3.958986	-2.416114	17.392190
H	-4.702517	-2.906776	17.658188
C	-2.869651	-3.034090	16.863116
H	-2.871389	-3.962485	16.804655
C	-1.773212	-2.353172	16.418812
H	-1.055850	-2.800919	16.030045
C	-1.758178	-0.965587	16.559118
H	-1.015364	-0.479217	16.278505
P	-5.253779	3.792256	17.685080
P	-2.971700	1.519763	17.263283
I	-6.860852	2.969861	14.703854
I	-3.967442	0.764602	14.065634
Pt	-4.707475	2.315851	16.081052
C	-6.354114	-1.620756	9.637319
H	-7.218162	-1.241674	9.412244
H	-6.517578	-2.469043	10.078701
I	-5.312654	-2.002700	7.841978
I	-5.428316	-0.356767	10.988064
C	-0.962549	-3.922431	0.009938
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C	-2.473284	-3.983942	-0.125691
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H	-2.758942	-4.883727	0.099384
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H	-4.177452	-2.984023	0.312767

C	-0.300362	-4.863700	-1.028916
H	-0.543383	-5.773498	-0.838917
H	0.654061	-4.772148	-0.982147
H	-0.600340	-4.630528	-1.911679
C	-2.744896	-1.603590	0.689841
H	-1.862832	-1.590716	1.069839
H	-3.322333	-1.035682	1.204300
H	-2.709031	-1.287450	-0.216306
C	1.182749	-3.084158	1.549220
C	1.106793	-1.789555	2.081217
H	0.380701	-1.554954	2.610290
C	2.097134	-0.855439	1.826911
H	2.052356	-0.005722	2.201062
C	3.165210	-1.207342	0.993839
H	3.825791	-0.582213	0.803841
C	3.245158	-2.466182	0.464766
H	3.961418	-2.689340	-0.084769
C	2.278166	-3.398868	0.733687
H	2.349092	-4.251446	0.371228
C	0.264609	-5.877925	1.891218
C	-0.705314	-6.863539	1.768450
H	-1.549246	-6.621784	1.464452
C	-0.475305	-8.161003	2.069524
H	-1.144041	-8.797575	1.964294
C	0.801586	-8.525780	2.548906
H	0.972205	-9.406968	2.797366
C	1.771266	-7.595955	2.648290
H	2.621210	-7.844862	2.931826
C	1.511593	-6.255577	2.323830

H	2.185744	-5.620435	2.405676
C	-4.741828	-2.600649	3.177363
C	-4.398709	-1.277437	3.528130
H	-3.538542	-0.954143	3.379054
C	-5.357011	-0.480648	4.089357
H	-5.126598	0.390527	4.320278
C	-6.624241	-0.896923	4.323201
H	-7.264068	-0.308988	4.659353
C	-6.944413	-2.210122	4.057203
H	-7.785747	-2.537707	4.276432
C	-6.014230	-3.038382	3.457977
H	-6.254110	-3.910987	3.241670
C	-4.339820	-5.265670	2.168908
C	-5.347594	-5.408720	1.233530
H	-5.596164	-4.672013	0.724918
C	-5.985019	-6.583161	1.037685
H	-6.643016	-6.658978	0.385844
C	-5.645991	-7.663189	1.812295
H	-6.091326	-8.471421	1.698296
C	-4.677409	-7.561623	2.733058
H	-4.455876	-8.301191	3.253363
C	-4.012351	-6.382891	2.920134
H	-3.334167	-6.329962	3.554437
P	-0.258163	-4.154887	1.719342
P	-3.490293	-3.670520	2.423214
I	0.641589	-3.884237	5.021549
I	-2.913521	-3.840749	5.795341
Pt	-1.558174	-3.817590	3.541137

1. E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170-173.

2. M. V. Vener, A. N. Egorova, A. V. Churakov and V. G. Tsirelson, *J. Comput. Chem.*, 2012, **33**, 2303–2309.