Electronic Supplementary Material (ESI) for Dalton Transactions.

Syntheses and Structures of N-alkyl Benzo-2,1,3-Selenadiazolium Cations, and Computational Investigation of their Supramolecular Aggregates

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Supplementary Information

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DFT Calculations. Optimized Cartesian Coordinates (Å) from PBE-D3 Calculations

4[5a]$_2$[I]$_2$

N	0.872865	0.962749	3.661278
Se	0.000000	0.000000	4.927608
C	0.491976	0.541303	2.453156
C	0.473964	0.535806	0.052705
H	0.814109	0.934520	-0.903020
C	0.960451	1.073158	1.216829
H	1.663544	1.905764	1.227607
N	-0.872865	-0.962749	3.661278
C	-0.491976	-0.541303	2.453156
C	-0.473964	-0.535806	0.052705
H	-0.814109	-0.934520	-0.903020
C	-0.960451	-1.073158	1.216829
H	-1.663544	-1.905764	1.227607
Se	-2.497763	-2.567041	4.798825
C	-4.392134	-4.665316	5.676814
H	-4.141460	-5.632924	6.131829
H	-4.382382	-4.788138	4.586832
H	-5.391453	-4.348910	6.006689
C	-1.538994	-3.003073	9.684610
H	-1.034594	-2.814464	10.631482
C	-3.265014	-4.223890	8.457833
H	-4.075799	-4.950296	8.433068
C	-2.592489	-3.946640	9.637200
H	-2.880863	-4.469172	10.548646
N	-3.397791	-3.672874	6.044234
N	-1.546714	-1.918660	6.175887
C	-2.880925	-3.533271	7.290243
C	-1.142195	-2.324996	8.548600
H	-0.328314	-1.600910	8.565567
C	-1.821314	-2.563688	7.328893
Se	2.497763	2.567041	4.798825
C	4.392134	4.665316	5.676814
H	4.141460	5.632924	6.131829
H	4.382382	4.788138	4.586832
H	5.391453	4.348910	6.006689
C	1.538994	3.003073	9.684610
H	1.034594	2.814464	10.631482
C	3.265014	4.223890	8.457833
H	4.075799	4.950296	8.433068
C	2.592489	3.946640	9.637200
H	2.880863	4.469172	10.548646
N	3.397791	3.672874	6.044234
N	1.546714	1.918660	6.175887
C	2.880925	3.533271	7.290243
C	1.142195	2.324996	8.548600
H	0.328314	1.600910	8.565567
C	1.821314	2.563688	7.328893
I	2.181406	4.656016	2.643828
I	-2.181406	-4.656016	2.643828

[5a][Cl] (iv)

Se	-3.665072	0.227816	2.408368
N	-2.486672	0.028134	1.012741
N	-5.023396	0.226757	1.061485
C	-4.513232	0.086210	-0.175687
C	-3.071990	-0.035832	-0.178540
C	-6.450209	0.343397	1.322032
H	-6.834163	1.270491	0.874944
H	-6.607523	0.363434	2.408459
H	-6.975308	-0.519487	0.891113
C	-5.233662	0.045700	-1.395055
H	-6.317878	0.141184	-1.405459
C	-2.375502	-0.201833	-1.411651
H	-1.287340	-0.283113	-1.390297
C	-4.520556	-0.110136	-2.565137
H	-5.058756	-0.139024	-3.512414
C	-3.101002	-0.231454	-2.577030
H	-2.588698	-0.346204	-3.531465
Cl	-5.356095	0.328400	4.436112

[5a][Br] (iv)

Se	-3.665072	0.227816	2.408368
N	-2.486672	0.028134	1.012741
N	-5.023396	0.226757	1.061485
C	-4.513232	0.086210	-0.175687
C	-3.071990	-0.035832	-0.178540
C	-6.450209	0.343397	1.322032
H	-6.834163	1.270491	0.874944
H	-6.607523	0.363434	2.408459
H	-6.975308	-0.519487	0.891113
C	-5.233662	0.045700	-1.395055
H	-6.317878	0.141184	-1.405459
C	-2.375502	-0.201833	-1.411651
H	-1.287340	-0.283113	-1.390297
C	-4.520556	-0.110136	-2.565137
H	-5.058756	-0.139024	-3.512414
C	-3.101002	-0.231454	-2.577030
H	-2.588698	-0.346204	-3.531465
Br	-5.408737	0.196519	4.609350

[5a][I] (iv)

Se	-3.457726	0.115592	0.000000
N	-2.222230	-1.251264	0.000000
N	-4.771402	-1.276948	0.000000
C	-4.218354	-2.504969	0.000000

C	-2.768152	-2.461816	0.000000
C	-6.199626	-1.005209	0.000000
C	-4.882058	-3.758298	0.000000
H	-5.968240	-3.819451	0.000000
C	-2.018642	-3.675245	0.000000
H	-0.928464	-3.614212	0.000000
C	-4.118849	-4.905362	0.000000
H	-4.620964	-5.872465	0.000000
C	-2.694825	-4.868641	0.000000
H	-2.139895	-5.805949	0.000000
H	-6.759146	-1.945207	0.000000
H	-6.463959	-0.408208	-0.881425
H	-6.463959	-0.408208	0.881425
I	-5.424522	2.439331	0.000000

[5a][Cl] (v)

Se	-1.389336	-1.579479	0.051096
N	-1.923816	-3.121343	0.786096
N	-2.984034	-1.763552	-1.140579
C	-3.657815	-2.874958	-0.851037
C	-3.035583	-3.611278	0.232360
C	-3.359657	-0.820692	-2.177722
H	-3.371360	-1.314054	-3.160409
H	-2.629877	-0.003221	-2.197505
H	-4.357568	-0.405084	-1.976335
C	-4.842264	-3.366705	-1.464560
H	-5.309806	-2.814371	-2.278683
C	-3.629303	-4.832322	0.671095
H	-3.153616	-5.375912	1.486040
C	-5.376187	-4.549115	-1.004930
H	-6.284304	-4.939265	-1.464701
C	-4.773626	-5.281542	0.059972
H	-5.235719	-6.211882	0.388340
Cl	0.547798	-1.443885	1.566117

[5a][Br] (v)

Se	-1.464627	-1.619175	0.031060
N	-1.985616	-3.166154	0.768907
N	-3.066389	-1.816145	-1.155354
C	-3.727501	-2.934779	-0.860438
C	-3.095690	-3.665625	0.220664
C	-3.467661	-0.886685	-2.195051
H	-3.468097	-1.384303	-3.175637
H	-2.758824	-0.050492	-2.220979
H	-4.474916	-0.495262	-1.991815
C	-4.909789	-3.437118	-1.468333
H	-5.386978	-2.891808	-2.281403
C	-3.677354	-4.890684	0.663685
H	-3.194337	-5.430372	1.476814
C	-5.432538	-4.623509	-1.004937
H	-6.339194	-5.020905	-1.461475
C	-4.820660	-5.350279	0.057557
H	-5.273302	-6.284472	0.388081
Br	0.616996	-1.447237	1.636567

[5a][I] (v)

Se	-1.612575	-1.675726	-0.0362941
N	-2.098362	-3.231670	0.7168931
N	-3.235395	-1.915115	-1.2037621
C	-3.867563	-3.043269	-0.8876021
C	-3.205507	-3.755132	0.1891551
C	-3.670244	-1.004797	-2.2450011
H	-3.661094	-1.506285	-3.2236011
H	-2.986163	-0.149520	-2.2789241
H	-4.686998	-0.640883	-2.0379821
C	-5.050008	-3.572495	-1.4736741
H	-5.548611	-3.041198	-2.2831181
C	-3.757816	-4.988652	0.6480711
H	-3.251490	-5.513155	1.4569321
C	-5.542339	-4.765709	-0.9955701
H	-6.447448	-5.183680	-1.4362691
C	-4.900544	-5.474074	0.0624171
H	-5.330035	-6.414595	0.4052541
I	0.663725	-1.440936	1.680151

$[5a]_2[Cl]_2$ (vi)

Se	-1.389336	-1.579479	0.051096
N	-1.923816	-3.121343	0.786096
N	-2.984034	-1.763552	-1.140579
C	-3.657815	-2.874958	-0.851037
C	-3.035583	-3.611278	0.232360
C	-3.359657	-0.820692	-2.177722
H	-3.371360	-1.314054	-3.160409
H	-2.629877	-0.003221	-2.197505
H	-4.357568	-0.405084	-1.976335
C	-4.842264	-3.366705	-1.464560
H	-5.309806	-2.814371	-2.278683
C	-3.629303	-4.832322	0.671095
H	-3.153616	-5.375912	1.486040
C	-5.376187	-4.549115	-1.004930
H	-6.284304	-4.939265	-1.464701
C	-4.773626	-5.281542	0.059972
H	-5.235719	-6.211882	0.388340
Se	1.389336	1.579479	-0.051096
N	1.923816	3.121343	-0.786096
N	2.984034	1.763552	1.140579
C	3.657815	2.874958	0.851037
C	3.035583	3.611278	-0.232360
C	3.359657	0.820692	2.177722
H	3.371360	1.314054	3.160409
H	2.629877	0.003221	2.197505
H	4.357568	0.405084	1.976335
C	4.842264	3.366705	1.464560
H	5.309806	2.814371	2.278683
C	3.629303	4.832322	-0.671095
H	3.153616	5.375912	-1.486040

C	5.376187	4.549115	1.004930
H	6.284304	4.939265	1.464701
C	4.773626	5.281542	-0.059972
H	5.235719	6.211882	-0.388340
Cl	0.547798	-1.443885	1.566117
Cl	-0.547798	1.443885	-1.566117

$[5a]_2[Br]_2$ **(vi)**

Se	-1.464627	-1.619175	0.031060
N	-1.985616	-3.166154	0.768907
N	-3.066389	-1.816145	-1.155354
C	-3.727501	-2.934779	-0.860438
C	-3.095690	-3.665625	0.220664
C	-3.467661	-0.886685	-2.195051
H	-3.468097	-1.384303	-3.175637
H	-2.758824	-0.050492	-2.220979
H	-4.474916	-0.495262	-1.991815
C	-4.909789	-3.437118	-1.468333
H	-5.386978	-2.891808	-2.281403
C	-3.677354	-4.890684	0.663685
H	-3.194337	-5.430372	1.476814
C	-5.432538	-4.623509	-1.004937
H	-6.339194	-5.020905	-1.461475
C	-4.820660	-5.350279	0.057557
H	-5.273302	-6.284472	0.388081
Se	1.464627	1.619175	-0.031060
N	1.985616	3.166154	-0.768907
N	3.066389	1.816145	1.155354
C	3.727501	2.934779	0.860438
C	3.095690	3.665625	-0.220664
C	3.467661	0.886685	2.195051
H	3.468097	1.384303	3.175637
H	2.758824	0.050492	2.220979
H	4.474916	0.495262	1.991815
C	4.909789	3.437118	1.468333
H	5.386978	2.891808	2.281403
C	3.677354	4.890684	-0.663685
H	3.194337	5.430372	-1.476814
C	5.432538	4.623509	1.004937
H	6.339194	5.020905	1.461475
C	4.820660	5.350279	-0.057557
H	5.273302	6.284472	-0.388081
Br	0.616996	-1.447237	1.636567
Br	-0.616996	1.447237	-1.636567

$[5a]_2[I]_2$ (vi)

Se	-1.612575	-1.675726	-0.036294
N	-2.098362	-3.231670	0.716893
N	-3.235395	-1.915115	-1.203762
C	-3.867563	-3.043269	-0.887602
C	-3.205507	-3.755132	0.189155
C	-3.670244	-1.004797	-2.245001
H	-3.661094	-1.506285	-3.223601
H	-2.986163	-0.149520	-2.278924
H	-4.686998	-0.640883	-2.037982
C	-5.050008	-3.572495	-1.473674
H	-5.548611	-3.041198	-2.283118
C	-3.757816	-4.988652	0.648071
H	-3.251490	-5.513155	1.456932
C	-5.542339	-4.765709	-0.995570
H	-6.447448	-5.183680	-1.436269
C	-4.900544	-5.474074	0.062417
H	-5.330035	-6.414595	0.405254
Se	1.612575	1.675726	0.036294
N	2.098362	3.231670	-0.716893
N	3.235395	1.915115	1.203762
C	3.867563	3.043269	0.887602
C	3.205507	3.755132	-0.189155
C	3.670244	1.004797	2.245001
H	3.661094	1.506285	3.223601
H	2.986163	0.149520	2.278924
H	4.686998	0.640883	2.037982
C	5.050008	3.572495	1.473674
H	5.548611	3.041198	2.283118
C	3.757816	4.988652	-0.648071
H	3.251490	5.513155	-1.456932
C	5.542339	4.765709	0.995570
H	6.447448	5.183680	1.436269
C	4.900544	5.474074	-0.062417
H	5.330035	6.414595	-0.405254
I	0.663725	-1.440936	1.680151
I	-0.663725	1.440936	-1.680151

$[5a]_2[Cl]_2$ **(vii)**

Se	-3.682894	0.150737	2.419853
N	-2.509747	0.014320	1.013066
N	-5.048977	0.160501	1.081319
C	-4.542785	0.068348	-0.161842
C	-3.098206	-0.013842	-0.176849
C	-6.476088	0.252855	1.351180
H	-6.886529	1.147207	0.863071
H	-6.619960	0.323424	2.436769
H	-6.982898	-0.642621	0.967137
C	-5.270018	0.046036	-1.378157
H	-6.356819	0.106786	-1.378904
C	-2.405724	-0.117197	-1.419510
H	-1.316239	-0.177511	-1.406045
C	-4.560534	-0.054864	-2.556108
H	-5.103910	-0.073672	-3.500720
C	-3.137804	-0.135989	-2.580749

H	-2.630628	-0.214034	-3.541604
Se	-0.137947	-0.076173	2.076557
N	-1.310453	0.062508	3.483708
N	1.228705	-0.086093	3.414400
C	0.723226	0.008049	4.657703
C	-0.721279	0.091761	4.673289
C	2.655531	-0.180456	3.143796
H	3.065097	-1.074954	3.632392
H	2.798682	-0.252053	2.058180
H	3.163764	0.714650	3.526797
C	1.451125	0.030753	5.873618
H	2.537849	-0.031328	5.873844
C	-1.412966	0.196974	5.916247
H	-2.502406	0.258001	5.903378
C	0.742369	0.133612	7.051830
H	1.286224	0.152657	7.996159
C	-0.680255	0.216262	7.077081
H	-1.186870	0.295791	8.038112
Cl	1.534280	-0.250514	0.058991
Cl	-5.356095	0.328400	4.436112

$[5a]_2[Br]_2$ (vii)

Se	-3.665072	0.227816	2.408368
N	-2.486672	0.028134	1.012741
N	-5.023396	0.226757	1.061485
C	-4.513232	0.086210	-0.175687
C	-3.071990	-0.035832	-0.178540
C	-6.450209	0.343397	1.322032
H	-6.834163	1.270491	0.874944
H	-6.607523	0.363434	2.408459
H	-6.975308	-0.519487	0.891113
C	-5.233662	0.045700	-1.395055
H	-6.317878	0.141184	-1.405459
C	-2.375502	-0.201833	-1.411651
H	-1.287340	-0.283113	-1.390297
C	-4.520556	-0.110136	-2.565137
H	-5.058756	-0.139024	-3.512414
C	-3.101002	-0.231454	-2.577030
H	-2.588698	-0.346204	-3.531465
Se	-0.155538	-0.150363	2.087810
N	-1.333421	0.050532	3.483620
N	1.202975	-0.151388	3.434455
C	0.693240	-0.010419	4.671775
C	-0.747821	0.113613	4.674793
C	2.629552	-0.270463	3.173580
H	3.012058	-1.198061	3.620868
H	2.786527	-0.291112	2.087108
H	3.156195	0.591675	3.604102
C	1.413909	0.028691	5.891035
H	2.497999	-0.068271	5.901234
C	-1.443906	0.280165	5.908043
H	-2.531965	0.362724	5.886888
C	0.701159	0.184919	7.061277
H	1.239492	0.212530	8.008513
C	-0.718228	0.308251	7.073356
H	-1.230283	0.423110	8.027912
Br	1.588217	-0.122052	-0.114157
Br	-5.408737	0.196519	4.609350

$[5a]_2[I]_2$ (vii)

Se	-3.457992	0.115532	0.000000
N	-2.222805	-1.251496	0.000000
N	-4.772032	-1.276649	0.000000
C	-4.219322	-2.504889	0.000000
C	-2.769111	-2.461966	0.000000
C	-6.200360	-1.004621	0.000000
C	-4.883378	-3.758193	0.000000
H	-5.969531	-3.819241	0.000000
C	-2.019890	-3.675586	0.000000
H	-0.929566	-3.614702	0.000000
C	-4.120251	-4.905403	0.000000
H	-4.622542	-5.872474	0.000000
C	-2.696209	-4.868932	0.000000
H	-2.141506	-5.806359	0.000000
Se	0.045311	-0.113517	0.000000
N	-1.189404	1.254112	0.000000
N	1.359726	1.277614	0.000000
C	0.807768	2.506255	0.000000
C	-0.642381	2.464164	0.000000
C	2.788155	1.004776	0.000000
C	1.472812	3.759093	0.000000
H	2.558967	3.819334	0.000000
C	-1.390710	3.678218	0.000000
H	-2.481011	3.618085	0.000000
C	0.710339	4.906696	0.000000
H	1.213269	5.873416	0.000000
C	-0.713734	4.871124	0.000000
H	-1.267667	5.808940	0.000000
I	2.009765	-2.436578	0.099905
I	-5.423475	2.437862	-0.099822
H	3.348298	1.944294	0.000000
H	3.052801	0.407708	-0.880765
H	3.050970	0.407430	0.882141
H	-6.760116	-1.944422	0.000000
H	-6.463713	-0.407469	-0.882129
H	-6.465554	-0.407757	0.880722

Table S1. Crystallographic Data for $[\mathbf{4}]_2[\mathbf{4}\text{-H}]_2][I][I_3]$ and $[\mathbf{4}]_2(C_6H_4(NH_2)_2H^+)_2][I]_2$. **Note:** these structures could not be fully refined due to their severely disordered iodine atoms. However, given their R int. values, the data are adequate to establish atom to atom connectivity and establish the composition of these crystals.

	$[\mathbf{4}]_2[\mathbf{4}\text{-H}]_2[I][I_3]$	$[\mathbf{4}]_2(C_6H_4(NH_2)_2H^+)_2][I]$
Chemical formula	$C_{18}H_{13}N_6I_4$	$C_{18}H_{16}N_6Se_2I$
Formula mass	820.95	601.18
Crystal system	monoclinic	triclinic
a	14.010(0)	10.037(1)
b	11.625(0)	10.623(1)
c	19.591(0)	19.605(2)
α	90	77.472(5)
β	104.262(1)	89.012(5)
γ	90	87.197(5)
Unit cell volume/Å^3	3092.2(1)	2038.1(4)
Temperature/K	100.15	296
Space group	P 1 21/n 1	P -1
Z	16	4
measured	5551	11876
No. independent reflections	4538	7715
R int	5.80	7.02
Final R_1 values ($I > 2\sigma(I)$)	0.0409	0.0527
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1009	.1176
Final R_1 values (all data)	0.0493	0.0959
Final $wR(F^2)$ values (all data)	0.1049	0.1375

ETS-NOCV Bonding Analysis

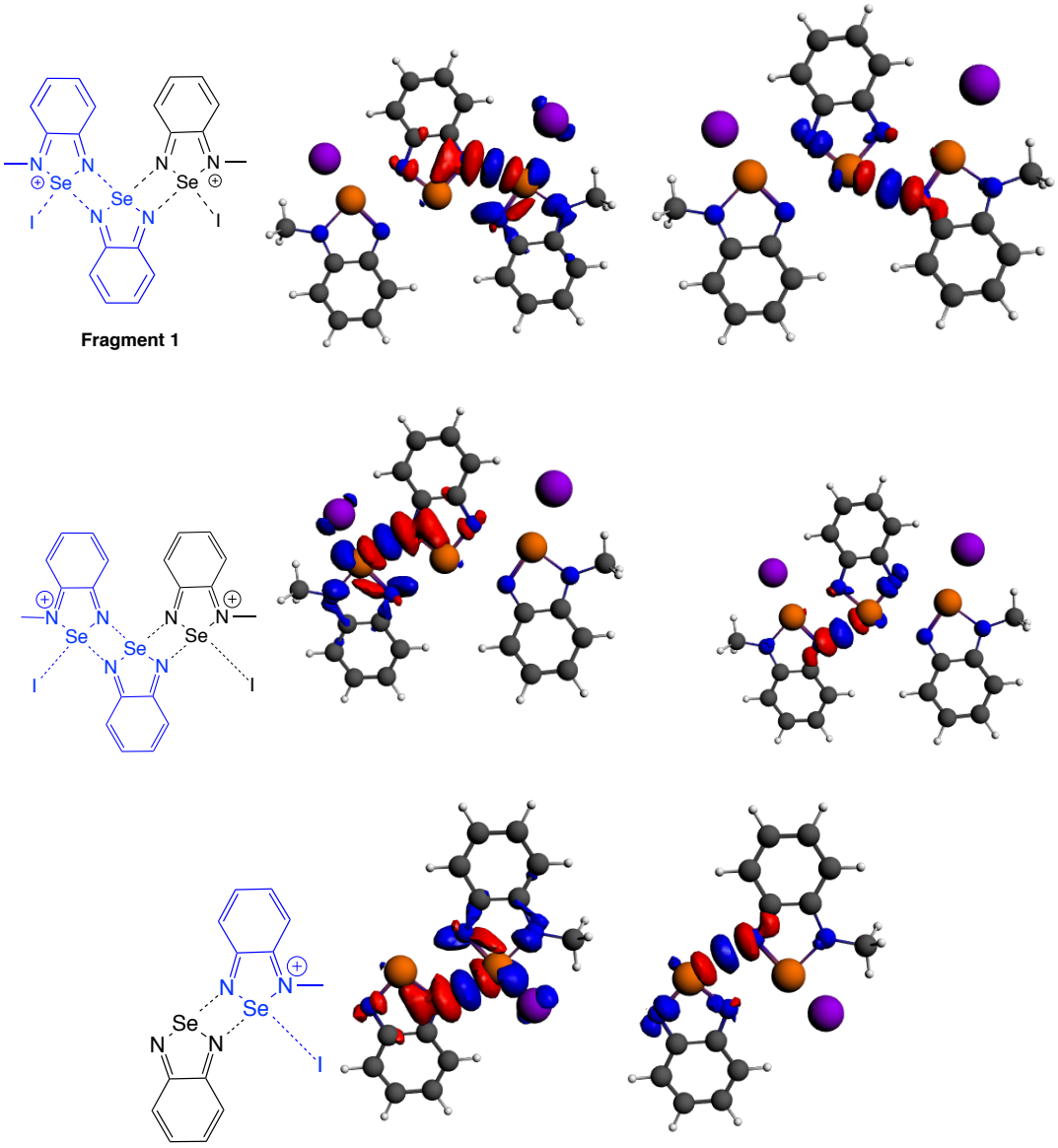

Figure S1. Deformation density (Δρ) isosurfaces (0.0008 a.u.) derived from the main contributing NOCVs (by energy) to the Se···N SBIs in the pseudo-trimer **4**[**5a**]$_2$[I]$_2$. Interacting fragments in the portioning scheme are denoted with different colour. In the isosurfaces, red colour indicates charge depletion while blue color denotes charge accumulation.