Supplementary data for the paper

EDA Complexes of *N*-halosaccharins with N- and O-donor ligands

by

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1. 1. Figures

Fig. S1
An ORTEP drawing of NISac·THF with thermal ellipsoids drawn at the 30% probability level.

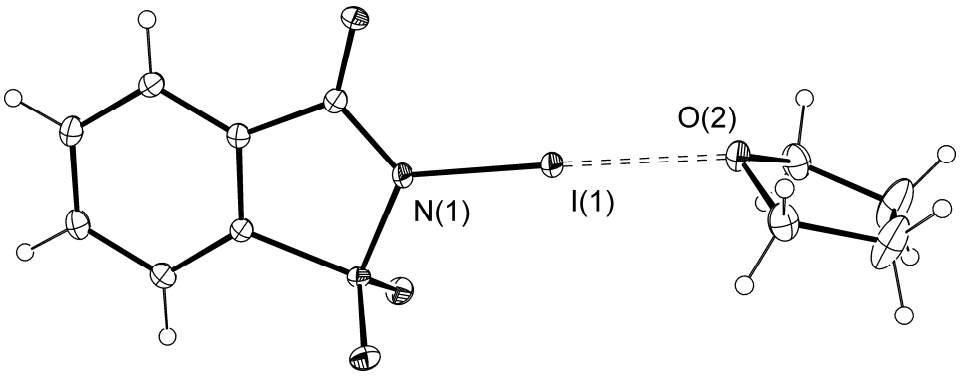


Fig. S2
An ORTEP drawing of NISac·Py with thermal ellipsoids drawn at the 30% probability level.

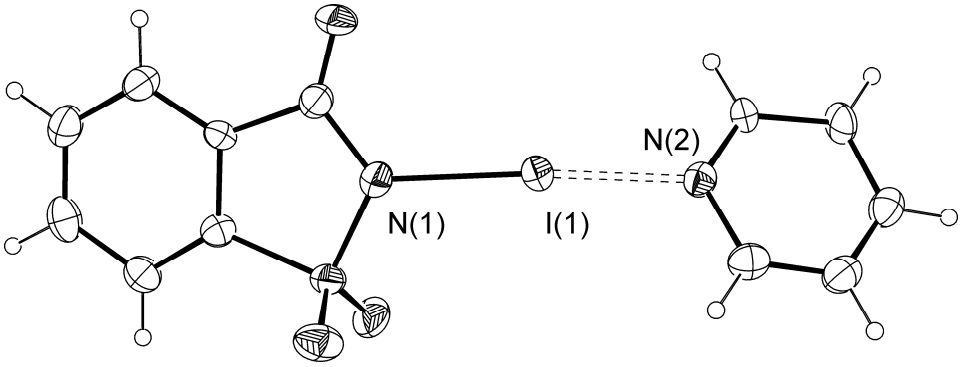


Fig. S3

An ORTEP drawing of $(NBSac)_2 \cdot Pyz$ with thermal ellipsoids drawn at the 30% probability level.

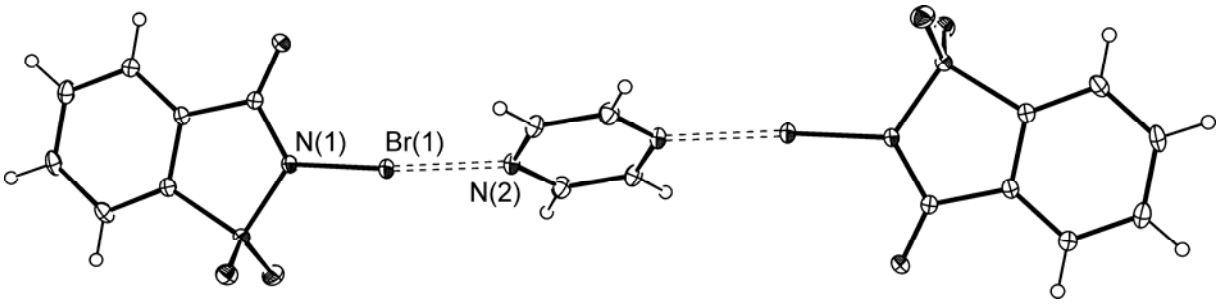
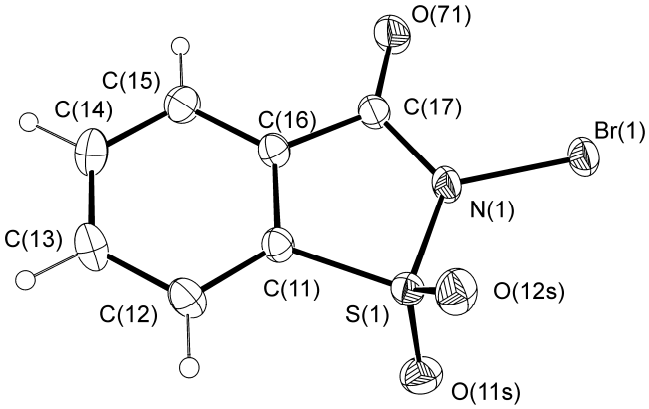


Fig. S4

ORTEP drawings of both molecules in the asymmetric unit of NBSac with thermal ellipsoids drawn at the 30% probability level.



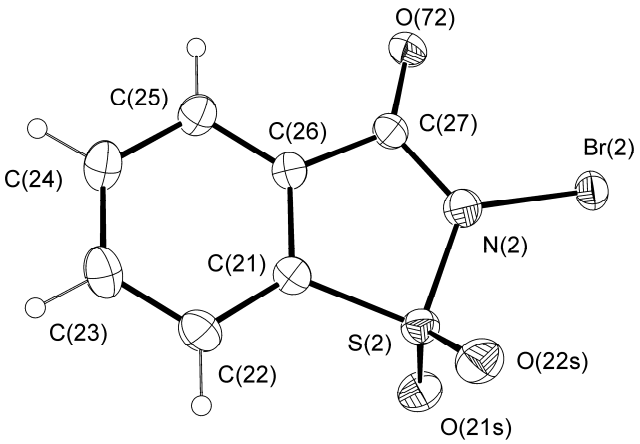


Fig. S5

A projection along the aromatic plane of the "non-planar" *N*-bromosaccharin molecule.

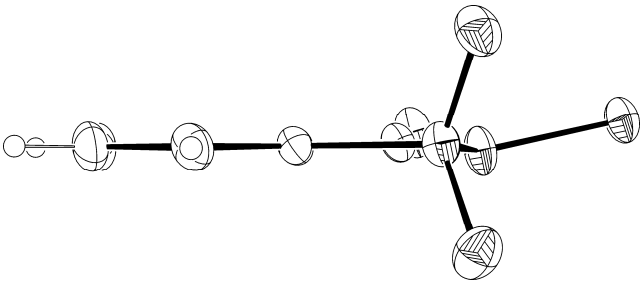


Fig. S6

A section of a layer in NISac·H_2O. The layers are perpendicular to the *c* axis. Each adduct forms four hydrogen bonds, drawn as dashed lines, with four adjacent adducts. Water molecule is engaged in hydrogen bonds with carbonyl [O(1)···O(7)^{i} = 2.770(3) Å] and sulfone oxygen [O(1)···O(2S)^{ii} = 2.820(3) Å] atoms. Symmetry codes: (i) –*x*+3/2, *y*+1/2, −*z*+3/2; (ii) –*x*+1/2, *y*+1/2, −*z*+3/2.

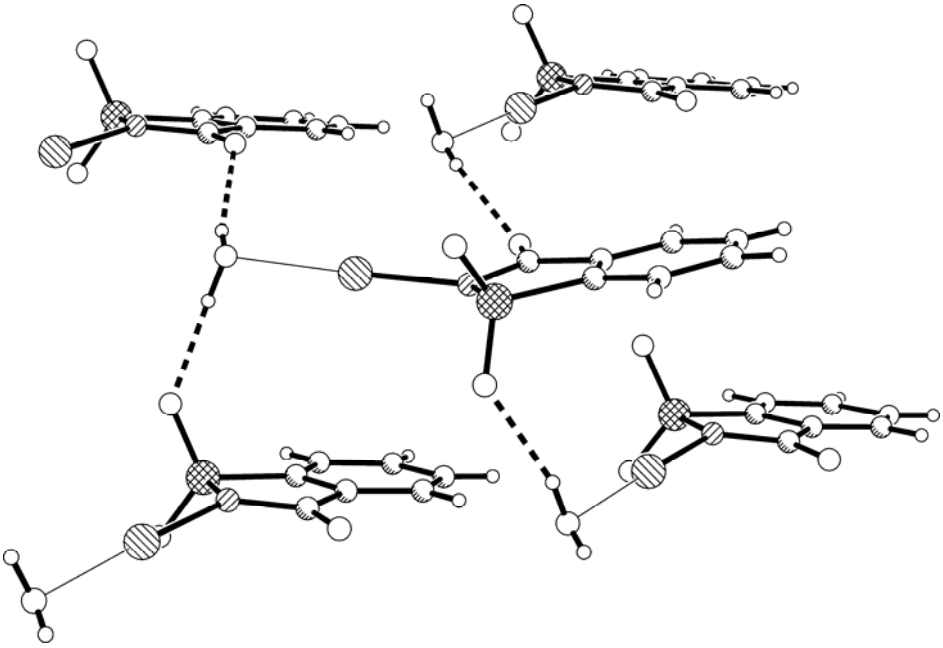
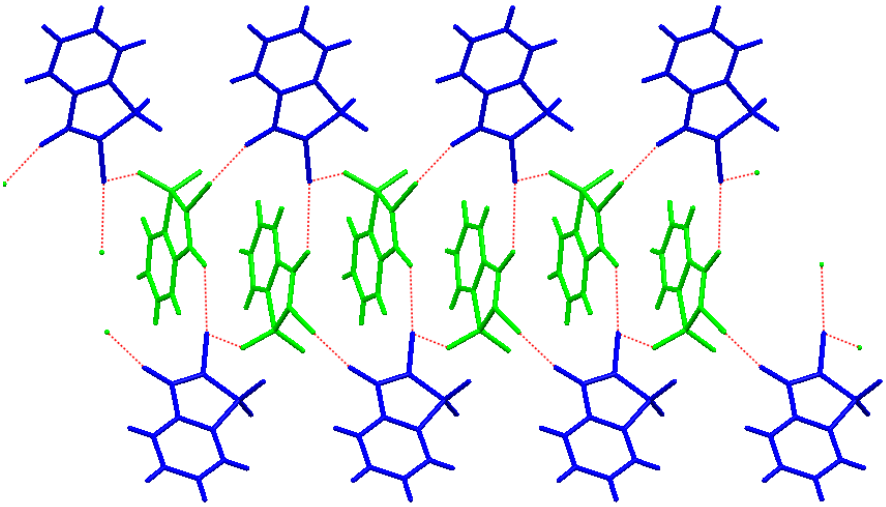


Fig. S7

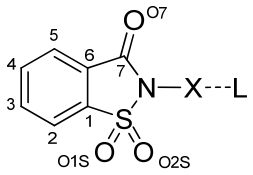
A section of a triple chain of "halogen-bonded" molecules in NBSac. Non-planar molecules of *N*-bromosaccharin are shown in green, whereas the planar ones are shown in blue. The chains propagate along the *a* axis.



1. 2. Listings of structural parameters for *N*-halosaccharin complexes and *N*-bromosaccharin

Table S1.

Bond lengths (Å) and angles (°) for NISac·H_2O, NISac·THF and NISac·Py [a]

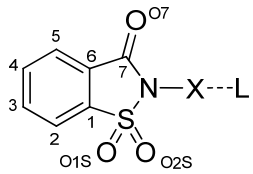


	NISac·H_2O	**NISac·THF**	**NISac·Py**
N−X	2.096(2)	2.073(2)	2.254(11)
X···L	2.443(2)	2.512(2)	2.279(11)
N−X···L	177.68(7)	178.51(9)	174.5(4)
C(7)−O(7)	1.215(3)	1.217(4)	1.178(16)
C(7)−N	1.386(3)	1.381(4)	1.392(16)
N−S	1.664(2)	1.664(3)	1.611(12)
C(7)−N−S	114.4(2)	115.7(2)	115.7(9)
S−O(1S)	1.431(2)	1.432(2)	1.406(11)
S−O(2S)	1.435(2)	1.432(2)	1.458(11)
O(1S)−S−O(2S)	116.2(1)	116.7(1)	116.6(7)
S−C(1)	1.756(2)	1.758(3)	1.758(13)
N−S−C(1)	93.6(1)	92.7(1)	94.8(6)

[a] Same atom labels are used as in the chart above.

Table S2.

Bond lengths (Å) and angles (°) for $(NISac)_2$·Pyz, $(NBSac)_2$·Pyz and NBSac [a]



	$(NISac)_2$·Pyz	**$(NBSac)_2$·Pyz**	**NBSac** [b]
N−X	2.142(2)	1.906(1)	1.847(2), 1.835(3)
X···L	2.423(2)	2.410(1)	–
N−X···L	175.26(6)	175.22(6)	–
C(7)−O(7)	1.214(3)	1.209(2)	1.201(3), 1.203(3)
C(7)−N	1.384(3)	1.387(2)	1.393(4), 1.379(4)
N−S	1.654(2)	1.664(2)	1.699(2), 1.699(3)
C(7)−N−S	114.6(1)	115.9(1)	115.6(2), 116.5(2)
S−O(1S)	1.428(2)	1.428(1)	1.416(2), 1.419(2)
S−O(2S)	1.436(2)	1.435(1)	1.422(2), 1.421(2)
O(1S)−S−O(2S)	116.8(1)	117.15(8)	117.6(2), 118.7(2)
S−C(1)	1.759(2)	1.757(2)	1.748(3), 1.759(3)
N−S−C(1)	93.76(9)	92.58(7)	91.3(1), 91.1(1)

[a] Same atom labels are used as in the chart above. [b] Two sets of parameters, one for each molecule in the asymmetric unit.

2. Computed geometries and enthalpies of halosaccharins and complexes

2.1 *xyz* coordinates of NISac and NBSac and their EDA complexes

MPW1K/6-311+G**

NBSac

C1	-4.0069812900	-0.7283380650	0.0002434897
C2	-3.9932903628	0.6593184056	0.0007631261
C3	-2.7993632691	1.3629745293	0.0011800760
C4	-1.6401766561	0.6233663734	0.0008620388
C5	-1.6365046132	-0.7554251653	0.0005784948
C6	-2.8265846058	-1.4517578243	0.0002302194
C7	-0.2831653071	-1.3597631878	0.0008350551
N8	0.6302656431	-0.3225115526	0.0054579589
S9	0.0044770662	1.2583878603	0.0008997726
O10	-0.0139617837	-2.5197392887	-0.0018691621
O11	0.3279407573	1.8991035911	-1.2359444979
O12	0.3252989809	1.9050679959	1.2352784808
Br13	2.4721452380	-0.6073476396	-0.0013606992
H14	-4.9512731341	-1.2484913678	-0.0000828608
H15	-4.9249360873	1.2016214840	0.0008470410
H16	-2.7815846732	2.4401546490	0.0016342884
H17	-2.8169217310	-2.5294355964	0.0000059272

NISac

C1	-4.2362000826	-0.6933632784	-0.0001604590
C2	-4.2234449126	0.6946114350	0.0000280750
C3	-3.0301559949	1.3988490979	0.0000417858
C4	-1.8709641340	0.6592164750	-0.0001203753
C5	-1.8659882845	-0.7184552827	-0.0002695188
C6	-3.0555550662	-1.4162224724	-0.0003084888
C7	-0.5093447230	-1.3153169095	-0.0002105914
N8	0.4127846036	-0.2852626336	0.0001451219
S9	-0.2236623941	1.2860863077	-0.0001218872
O10	-0.2425903793	-2.4776541112	-0.0003587072
O11	0.0959016682	1.9343009545	-1.2355623027
O12	0.0957729117	1.9347536750	1.2351131856
I13	2.4171304362	-0.6040747047	0.0002921021
H14	-5.1804202298	-1.2138166126	-0.0001613995
H15	-5.1555928652	1.2361722272	0.0001810299
H16	-3.0123054847	2.4760079323	0.0001963352
H17	-3.0457647922	-2.4938997516	-0.0004135343

NISac·Py

C1	-4.5941117715	-0.8696632007	-0.2040648850
C2	-4.6806306281	0.4912730450	0.0573511365
C3	-3.5408107836	1.2636593956	0.2111597263
C4	-2.3311421098	0.6199428196	0.0926968011
C5	-2.2292790659	-0.7271187593	-0.1653968091
C6	-3.3645185683	-1.4943549957	-0.3183273188
C7	-0.8252941004	-1.2066131132	-0.2508052409
N8	0.0256477498	-0.1516118740	-0.0397373294
S9	-0.7167657412	1.3212357552	0.2327594962
O10	-0.4901039767	-2.3363684174	-0.4684897578
O11	-0.4431978141	2.2207392868	-0.8523976856
O12	-0.4552690346	1.7682884735	1.5717528442
H13	-5.4985580667	-1.4452831737	-0.3190775171
H14	-5.6495302235	0.9563977723	0.1423218683
H15	-3.6003755392	2.3201414877	0.4139114848
H16	-3.2740737522	-2.5490336446	-0.5205429258
I17	2.1193561436	-0.3426954688	-0.0874989012
C18	7.3373403228	-0.8962386490	-0.1832045002
C19	6.7706727780	0.3644635194	-0.1833358459
C20	5.3947212332	0.4688506902	-0.1625667684
N21	4.6046290979	-0.5948298555	-0.1422649753
C22	5.1443385189	-1.8052930111	-0.1420395088
C23	6.5100111955	-2.0034115483	-0.1623312259
H24	8.4091476925	-1.0145179270	-0.1990485701
H25	7.3777651097	1.2540506916	-0.1992282659
H26	4.9038882423	1.4302411493	-0.1617180803
H27	4.4548417800	-2.6357868625	-0.1251513848
H28	6.9089901425	-3.0039024920	-0.1616798572

NISac·Py (B3LYP/6-311+G)**

C1	-4.6664821898	-0.8671649813	-0.2050919648
C2	-4.7554723115	0.5013482150	0.0687610471
C3	-3.6058869145	1.2778325722	0.2270843867
C4	-2.3879420242	0.6315791737	0.1005372329
C5	-2.2793901180	-0.7243553971	-0.1695636701
C6	-3.4262150616	-1.4936163675	-0.3271039505
C7	-0.8671135440	-1.2142957550	-0.2638346282
N8	0.0028296208	-0.1611710582	-0.0416993796
S9	-0.7516668110	1.3501083629	0.2459177295
O10	-0.5399757249	-2.3592173264	-0.4969239797
O11	-0.4773942930	2.2686954424	-0.8533514191
O12	-0.4855141497	1.7961203223	1.6087200788
H13	-5.5744167266	-1.4468095922	-0.3236626384
H14	-5.7287919719	0.9688920818	0.1597802482
H15	-3.6658454436	2.3381231133	0.4386303999
H16	-3.3375034871	-2.5523547063	-0.5388020492
I17	2.1358209917	-0.3558297612	-0.0930934820
C18	7.4317713662	-0.8993751182	-0.1768954013
C19	6.8571594239	0.3683194048	-0.1947178625
C20	5.4708003435	0.4732110566	-0.1785414773
N21	4.6740211989	-0.6017262764	-0.1460520503
C22	5.2239426721	-1.8221922644	-0.1295553392
C23	6.6005050279	-2.0154705025	-0.1438408591
H24	8.5093297838	-1.0158238697	-0.1886436360
H25	7.4659534647	1.2632397590	-0.2207575943
H26	4.9768138813	1.4385892565	-0.1903647064
H27	4.5347930895	-2.6591986351	-0.1035759758
H28	7.0050465319	-3.0196708093	-0.1295738440

NISac·THF

C1	-4.5288935813	-0.8042527980	-0.5325144435
C2	-4.6184985678	0.5605648434	-0.2964647692
C3	-3.4862847458	1.3200344417	-0.0514068983
C4	-2.2794383894	0.6598192030	-0.0533700274
C5	-2.1753657303	-0.6927995954	-0.2854122544
C6	-3.3035483350	-1.4465451134	-0.5296866017
C7	-0.7812763004	-1.1981666930	-0.2401607364
N8	0.0622075572	-0.1445734639	0.0371203275
S9	-0.6818284051	1.3521186647	0.2259897764
O10	-0.4399955892	-2.3293692662	-0.4145984225
O11	-0.2990274509	2.2244419710	-0.8451495399
O12	-0.5401888894	1.8032253238	1.5785593576
H13	-5.4275754892	-1.3691251321	-0.7198717888
H14	-5.5842999790	1.0391465973	-0.3032278951
H15	-3.5496921021	2.3792548165	0.1329077808
H16	-3.2111217422	-2.5047454097	-0.7098850876
I17	2.1069913052	-0.3786882833	0.1985917680
O18	4.6738392513	-0.7297926666	0.3479685396
C19	5.5203991948	0.2999313977	-0.1320897517
H20	4.9917282745	1.2409321756	-0.0333046701
H21	6.4143797809	0.3335537151	0.4916935421
C22	5.1877061185	-1.9364726013	-0.1873964286
H23	4.4157598401	-2.6934378746	-0.1096081220
H24	6.0452065886	-2.2465911595	0.4114036838
C25	5.5946807182	-1.5984424352	-1.6150279891
H26	6.4657096486	-2.1660392838	-1.9263489466
H27	4.7870432420	-1.8266007882	-2.3033230236
C28	5.8555529612	-0.0839777354	-1.5695526216
H29	5.2088672508	0.4378020349	-2.2674888960
H30	6.8813050603	0.1705565255	-1.8163022797

NISac·H_2O

C1	-4.4871668308	-0.8355514207	0.0390920043
C2	-4.5510169962	0.5511736532	0.0241278333
C3	-3.3986533659	1.3200602052	0.0016519554
C4	-2.1999391200	0.6460114910	-0.0046305956
C5	-2.1197954933	-0.7280031111	0.0099946966
C6	-3.2682002006	-1.4911504334	0.0321232230
C7	-0.7292594044	-1.2438224047	0.0004943022
N8	0.1378058344	-0.1731946947	-0.0204630899
S9	-0.5833692464	1.3505177400	-0.0322933730
O10	-0.4052573988	-2.3939319320	0.0101720427
O11	-0.3199911049	2.0076567991	-1.2778109436
O12	-0.2903331776	2.0379333266	1.1905765650
H13	-5.4011504185	-1.4073207561	0.0564535438
H14	-5.5119220919	1.0399201013	0.0299852320
H15	-3.4406558236	2.3964522525	-0.0103334570
H16	-3.1968021127	-2.5664211379	0.0435312869
I17	2.1765101131	-0.3952646683	-0.0304156817
O18	4.8653398439	-0.7552431580	-0.0279767067
H19	5.2360379993	-1.5627355121	-0.3703025715
H20	5.3987236911	-0.4945825766	0.7164183220

$(NISac)_2$·Pyz

C1	-9.3110354387	1.0570770779	-1.3760241085
C2	-10.6123713299	0.8206599777	-0.9331640978
C3	9.7606512340	0.4245014452	-1.0260629806
C4	0.6658339038	-0.0458844086	-1.1247552669
C5	-6.8053255308	0.6976301057	-0.9380528769
C6	-8.2576236610	0.5498218707	-0.6336650916
C7	-0.7139169432	-0.0572220209	-1.0809288528
C8	8.5018523744	0.1756462699	-0.5557118530
C9	10.8119459031	-0.0789681315	-0.2825327911
C10	-10.8515373137	0.0932721471	0.2241096405
C11	-8.5098134641	-0.1699944884	0.5111760494
C12	8.2683409997	-0.5368521877	0.5971811664
C13	10.5926741826	-0.7994579977	0.8817502800
C14	-9.7952381368	-0.4188968571	0.9713906899
C15	6.8314793526	-0.6874278887	0.9194301454
C16	9.3161148974	-1.0366075925	1.3349694462
C17	0.7373367914	-0.0011966241	1.1390577640
C18	-0.6418421461	-0.0113876659	1.1824297402
H19	-9.1028149877	1.6188387129	-2.2725355394
H20	-11.4545426767	1.2065621111	-1.4936488504
H21	9.9218041565	0.9853480383	-1.9303284809
H22	1.1980184094	-0.0598753795	-2.0618905849
H23	-1.3053758175	-0.0784405328	-1.9819930260
H24	11.8165432293	0.0916526257	-0.6139167261
H25	-11.8748313389	-0.0760579813	0.5482991455
H26	11.4316355952	-1.1789621646	1.4392807271
H27	-9.9718219990	-0.9854337041	1.8717151206
H28	9.1224377641	-1.5938158328	2.2346220701
H29	1.3281854893	0.0208721382	2.0403851529
H30	-1.1744811694	0.0025401762	2.1193526817
N31	6.0965546072	-0.0479470958	-0.0503811724
N32	1.3798550209	-0.0185105208	-0.0136507453
N33	-6.0731996732	0.0557796937	0.0378319430
N34	-1.3564089111	-0.0402704366	0.0723947661
O35	6.7367327465	0.0170260458	-2.5157162680
O36	-6.3362819405	1.2785269896	-1.8742773128
O37	6.8251652753	2.1062128437	-1.2256738404
O38	-6.8269343421	-2.1129476722	1.1656177162
O39	6.3846218824	-1.2674502354	1.8623854328
O40	-6.7476306733	-0.0209316212	2.5024635113
S41	6.9789321348	0.6841360995	-1.2780663873
S42	-6.9828157493	-0.6858435892	1.2410214007
I43	4.0284297066	-0.0199475579	-0.0511411665
I44	-4.0019253436	-0.0089060262	0.0809526479

$(NBSac)_2$·Pyz

C1	10.2117194481	-0.3362710428	-2.1492194377
C2	8.9729954100	0.2788781666	-2.2015913075
C3	10.3728926010	-1.5622810598	-1.5189424819
C4	7.9042324143	-0.3605076474	-1.6110302495
C5	6.5087086738	0.1397851204	-1.5676247143
C6	9.3003247279	-2.2073652220	-0.9245482859
C7	8.0798671276	-1.5772772624	-0.9903441016
C8	0.5001551375	-1.3127511803	-0.3370558280
C9	-0.8631308000	-1.1491098713	-0.1651909014
C10	-9.2202342575	2.3119000916	1.0593579315
C11	-8.0409849495	1.6048101934	1.0481711985
C12	0.8090334170	0.9022162681	0.0062270705
C13	-0.5541018919	1.0658898022	0.1781455752
C14	-10.3098221216	1.7061031102	1.6639447183
C15	-7.9212319210	0.3498363341	1.6025127957
C16	-6.5616652754	-0.2312602645	1.4847044463
C17	-10.2048093600	0.4423152665	2.2280706139
C18	-9.0070772839	-0.2508971202	2.2025569790
H19	11.0647199339	0.1417863063	-2.6037390457
H20	8.8264382440	1.2306514667	-2.6858917280
H21	11.3472690947	-2.0227378159	-1.4901225514
H22	9.4180794529	-3.1593153383	-0.4338746299
H23	0.9288795854	-2.2805758834	-0.5466881221
H24	-1.5433123208	-1.9838772768	-0.2342050841
H25	-9.2938777153	3.2926690210	0.6196193285
H26	-11.2530644157	2.2271978839	1.6957523343
H27	1.4892910528	1.7369337487	0.0754160187
H28	-0.9830091280	2.0335876845	0.3883387136
H29	-11.0697252532	-0.0037329413	2.6924191872
H30	-8.9047798009	-1.2329324837	2.6349835389
N31	5.7468879431	-0.7845446357	-0.8901965128
N32	1.3261695393	-0.2858826175	-0.2497858755
N33	-1.3801280845	0.0389529325	0.0912353044
N34	-5.7684795522	0.6750222293	0.8188733425
O35	6.1084734272	1.1627762726	-2.0352061147
O36	-6.5613500553	2.2125052702	-1.0667522847
O37	6.0786864757	-3.3155358227	-1.0341768407
O38	-5.9312341210	3.2099528453	1.1009908588
O39	6.5589671503	-2.1723038685	1.0999060464
O40	-6.2090917042	-1.2959698456	1.8938345831
S41	6.5496856050	-2.1586992872	-0.3326244886
S42	-6.5011622311	2.1232142375	0.3616509884
Br43	3.8817915196	-0.5776206389	-0.6109703224
Br44	-3.9208514203	0.3892558302	0.4946646240

2.2 Computed X–L and N–X bond lengths and total enthalpies

Table S3. Computed X–L and N–X bond lengths and total enthalpies of NISac and NBSac and their EDA complexes[a]

Compound	Method	d(X···L) Å	d(N–X) Å	H_{tot} /Hartree [b]
NISac·H_2O	B	2.789	2.081	-1035.559789
NISac·H_2O	M	2.713	2.051	-1035.645750
NISac·H_2O	B (sol)[c]	2.707	2.105	–
NISac·H_2O	M (sol)[c]	2.592	2.080	–
NISac·THF	B	2.640	2.097	-1191.524731
NISac·THF	M	2.588	2.063	-1191.645162
NISac·Py	B	2.551	2.142	-1207.393259
NISac·Py	M	2.499	2.103	-1207.505438
NISac·Py	B (sol)[c]	2.361	2.282	–
NISac·Py	M (sol)[c]	2.307	2.232	–
$NISac_2$·Pyz	B	2.670	2.107	-2182.565658
$NISac_2$·Pyz	M	2.646	2.073	-2182,760659
$NBSac_2$·Pyz	B	2.614	1.944	-2186.089387
$NBSac_2$·Pyz	M	2.596	1.897	-2186.286242
NISac	B	–	2.060	-959.117159
NISac	M	–	2.029	-959.208636
NBSac	B	–	1.900	-960.882790
NBSac	M	–	1.864	-960.973866
H_2O	B	–	–	-76.433395
H_2O	M	–	–	-76.427494
THF	B	–	–	-232.396225
THF	M	–	–	-232.423884
Py	B	–	–	-248.257113
Py	M	–	–	-248.276419
Pyz	B	–	–	-264.305637
Pyz	M	–	–	-264.316875

[a] (B) B3LYP or (M) MPW1K/6-311+G** in vacuum. [b] Total enthalpy at 25 °C. [c] Geometry optimized in solution in DMSO.