Electronic supporting information for:

Halogen Bonding Based "Catch and Release": Reversible Solid State Entrapment of Elemental Iodine with Mono-Alkylated DABCO Salts

Anssi Peuronen[a], Arto Valkonen[b], Minna Kortelainen[b], Kari Rissanen[b] and Manu Lahtinen[a*]

[a] *Department of Chemistry, University of Jyväskylä, P.O.Box 35, FIN-40014 University of Jyväskylä, Finland.*

[b] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O.Box 35, FIN-40014 University of Jyväskylä, Finland.*

*Corresponding author: E-mail: manu.k.lahtinen@jyu.fi

Table S1. Experimental (single crystal X-ray) N···I and I–I distances (Å) with standard deviations.

	Experimental	
	N···I	I–I
1a	2.366(3)	2.8536(4)
1a·$CHCl_3$	2.383(4)	2.8442(4)
1b		
N1···I1,N2···I3; I1—I2,I3—I4	2.427(12), 2.417(12)	2.837(3), 2.828(3)
N1A···I1A, N2A···I3A; I1A—I2A, I3A—I4A	2.422(10), 2.424(10)	2.827(3), 2.835(3)
N1B···I1B, N2B···I3B; I1B—I2B, I3B—I4B	2.409(10), 2.429(10)	2.827(2), 2.829(3)
[**2**···I_2]PF_6	2.4790(78)	2.8009(10)
[**3**···I_2]PF_6	2.5185(90)	2.7791(11)
[**4**···I_2]PF_6	2.5321(59)	2.7682(6)
[**5**···I_2]PF_6	2.5429(38)	2.7688(4)
[**6**···I_2]PF_6	2.5449(50)	2.7680(6)
[**7**···I_2]PF_6	2.5425(49)	2.7670(5)

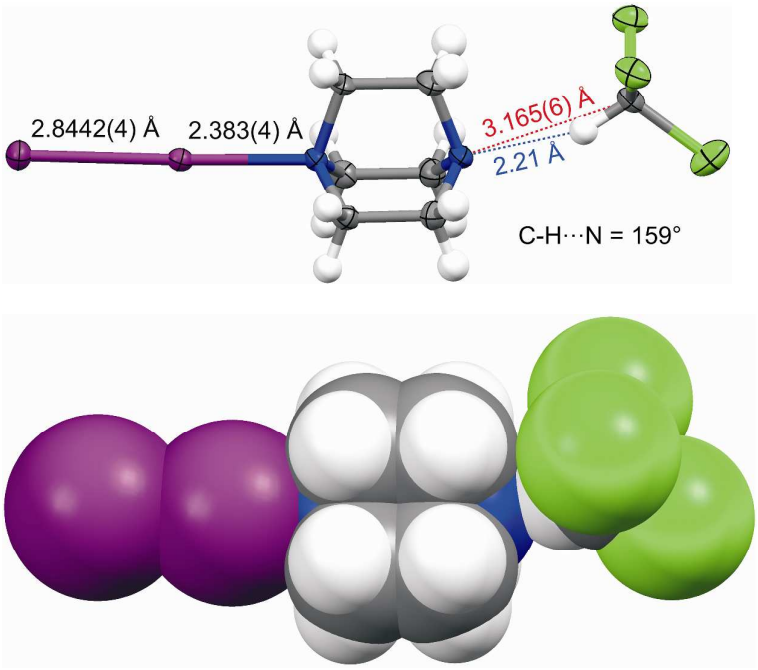

Fig. S1. Crystallographic diagram of **1a**·$CHCl_3$ showing the thermal ellipsoids (50 % probability) with selected geometric parameters (above) and spacefill presentation (below).

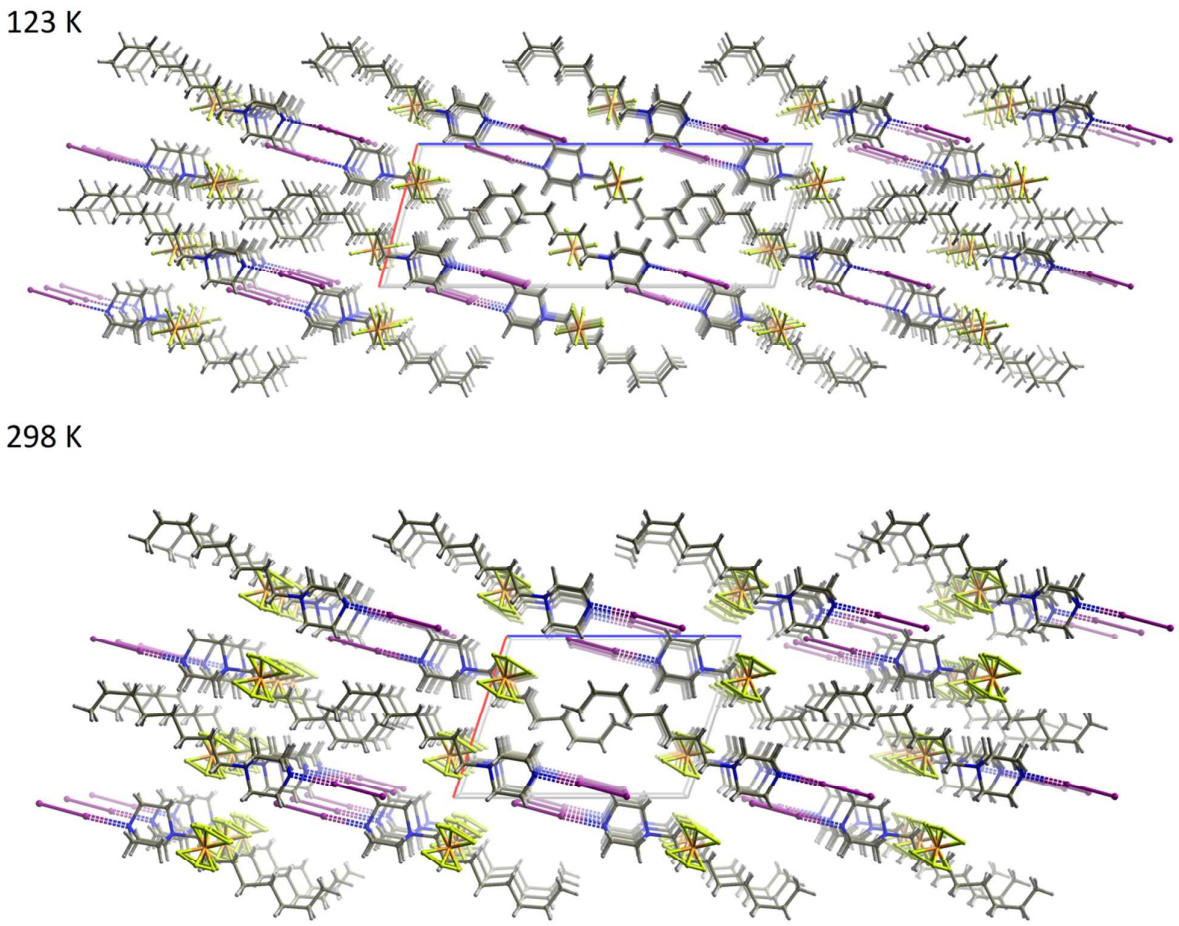

Fig. S2. Comparison between the single crystal structures of [**3**···I_2]PF_6 recorded at 123 K and 298 K. The alkyl chains in 123 K data and PF_6^- anions in 298 K data are disordered. Unit cell parameters for room temperature measurement are: a = 9.996(5), b = 8.762(5), c = 13.644(5), β = 108.112(5), V = 1135.8(10), monoclinic $P2_1/m$ and for low temperature measurement: a = 9.9339(6), b = 8.5824(6), c = 26.3690(15), β = 104.980(4), V = 2171.7(2), monoclinic $P2_1/c$.

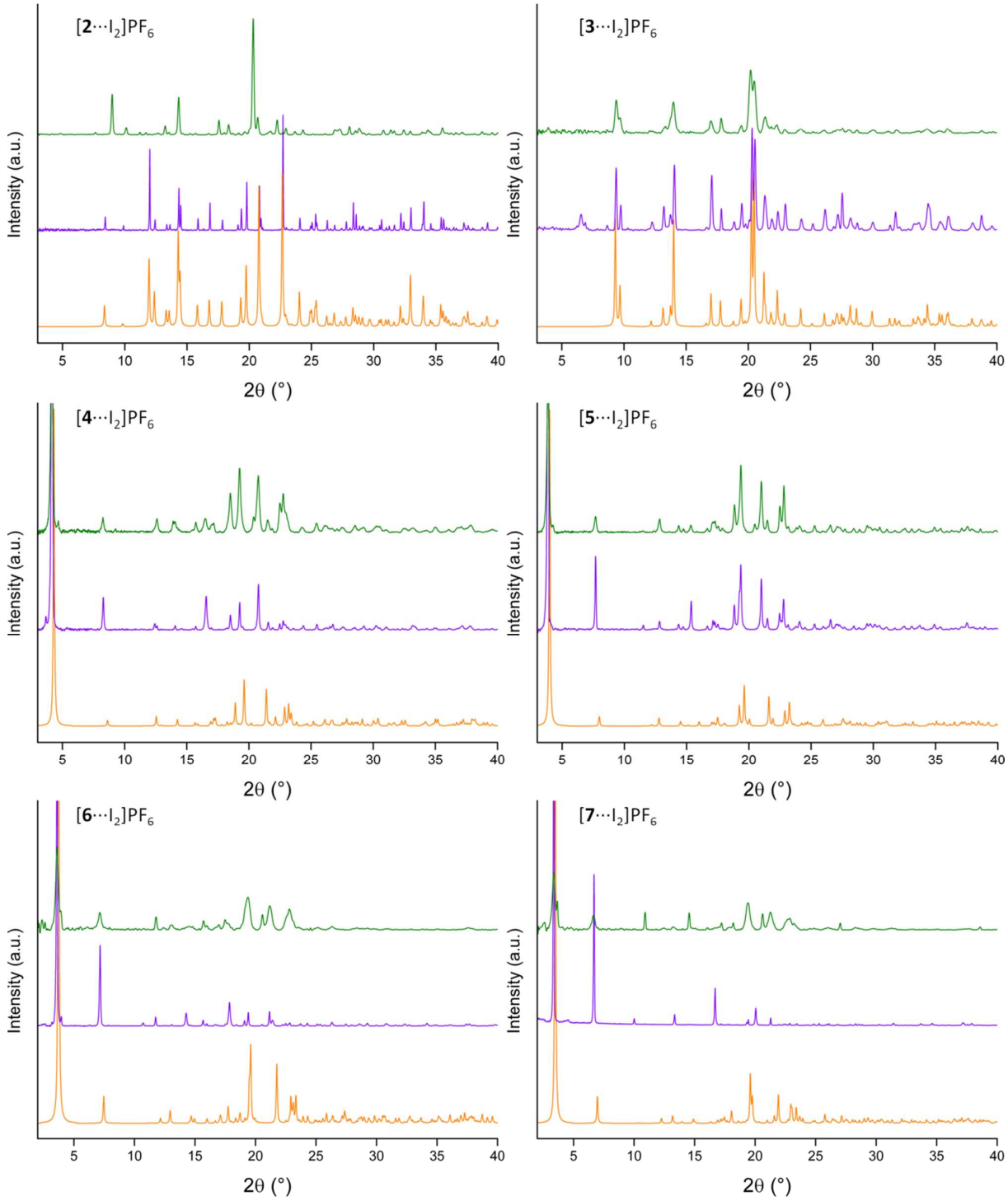

Fig. S3. PXRD measurements of bulk powders [**2**···I_2]PF_6 – [**7**···I_2]PF_6 obtained via solid state (upper graph, green) and solution (middle graph, violet) reactions compared to calculated patterns generated from corresponding single crystal data (lower graph, orange).

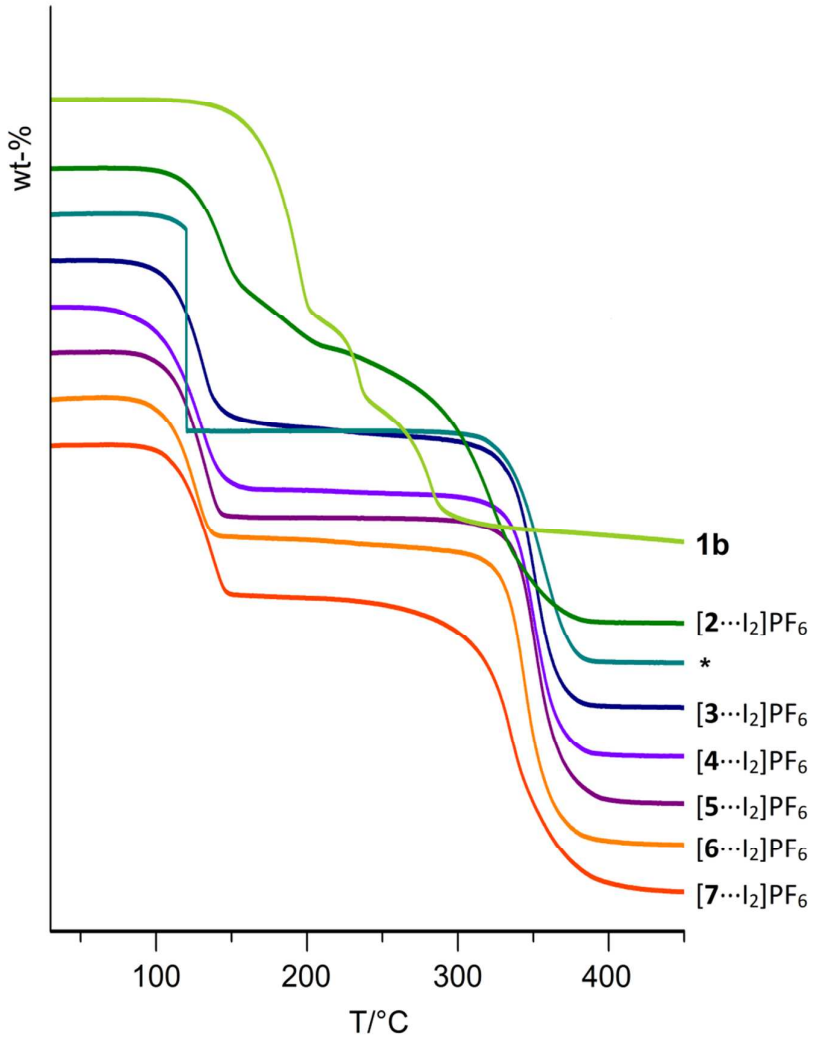

Fig. S4. TG measurements of synthesized I_2-complexes. (*) measurement of [**2**···I_2]PF_6 including a 60 min isothermal step at 110 °C.

Table S2. Phase transition, melting and decomposition temperatures ($T_{c\text{-}c}$, T_m and T_{dec} respectively) for **2**PF_6 – **7**PF_6 derived from DSC measurements. Enthalpies for corresponding events are in parenthesis.

	$T_{c\text{-}c}$ (°C) and ΔH (kJ mol^{-1})	T_m (°C) and ΔH (kJ mol^{-1})	T_{dec}(°C)
2PF_6	121.7 (11.4)		307.3
3PF_6	98.4 (9.5)	139.4 (11.6)	294.8
4PF_6	69.9 (17.3)	159.7 (6.4)	308.0
5PF_6	86.4 (26.1)	166.9 (8.4)	295.1
6PF_6	93.9 (32.8)	181.3 (8.3)	310.8
7PF_6	104.1 (39.1)	186.6 (7.2)	267.5

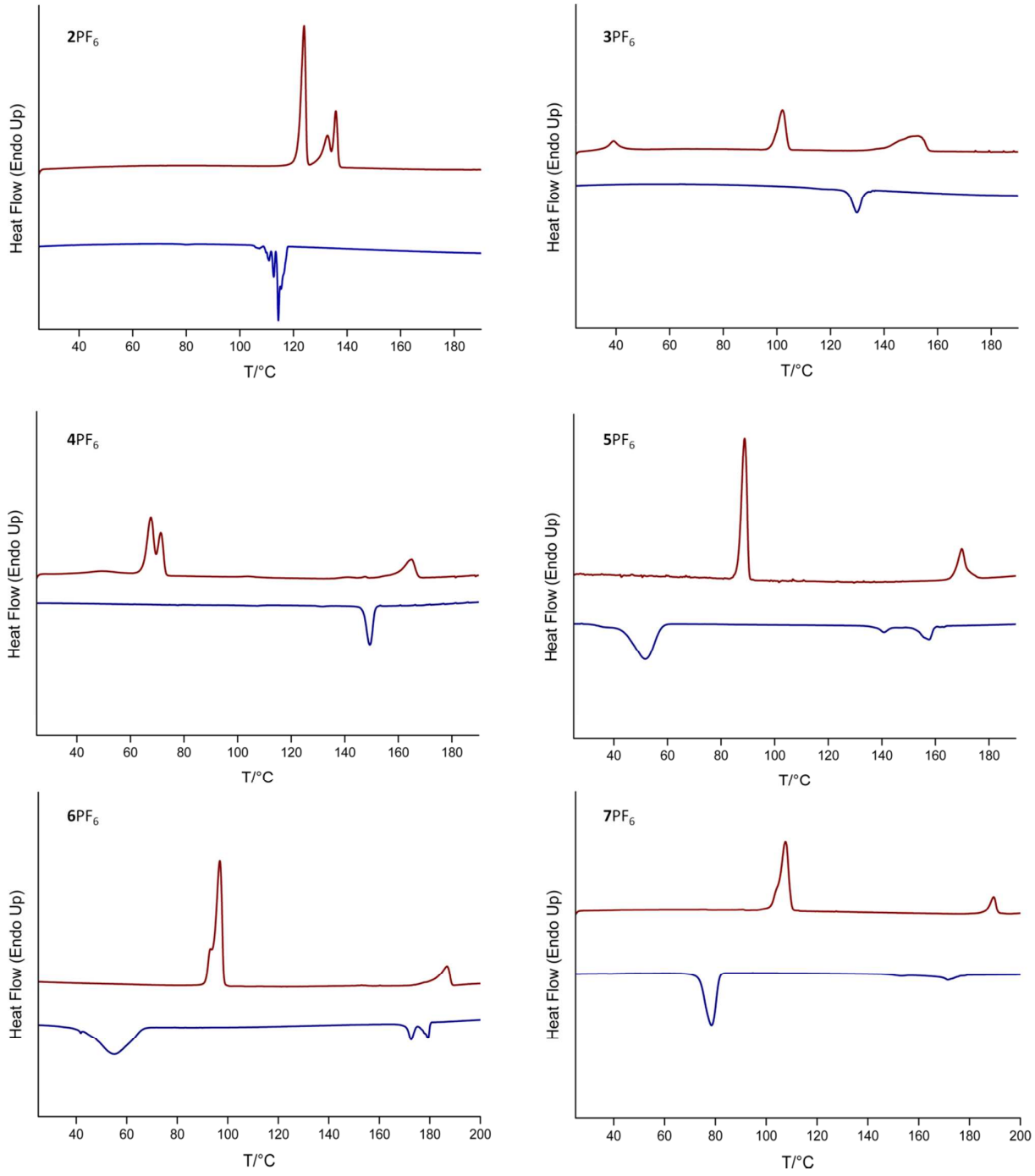

Fig. S5. DSC measurements of **2**PF_6 – **7**PF_6 showing single heating-cooling cycle graphs (heating with red and cooling with blue line). Heating-cooling cycles were repeated for each sample producing virtually identical thermal events on both heating scans. Calculated transition temperatures and enthalpies are reported in table S2.

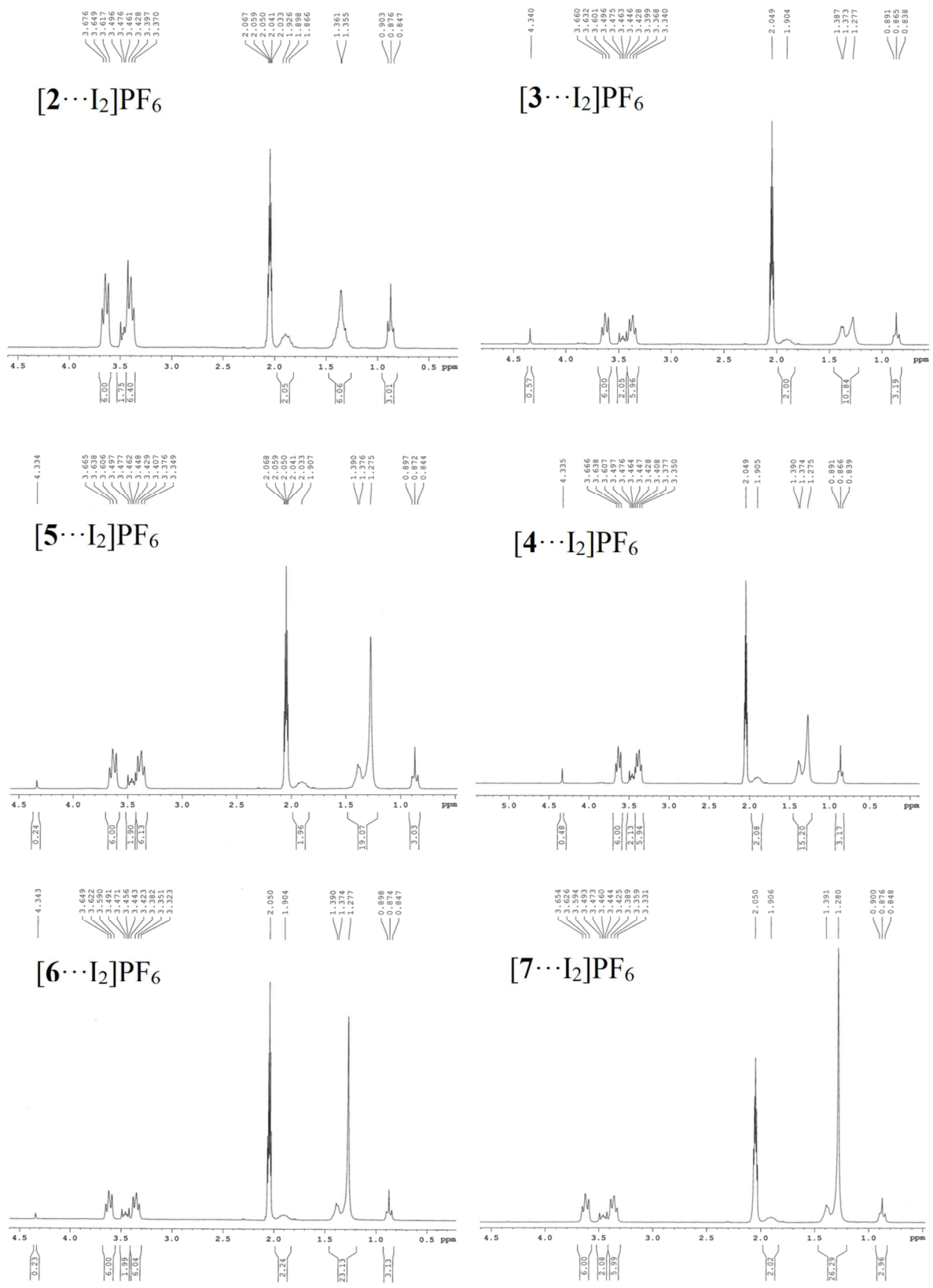

Fig. S6. ^{1}H NMR data of complexes [**2**···I_2]PF_6 – [**7**···I_2]PF_6. Measurements were carried out with Bruker Avance 250 NMR spectrometer at 30°C using acetone-d_6 as a solvent.

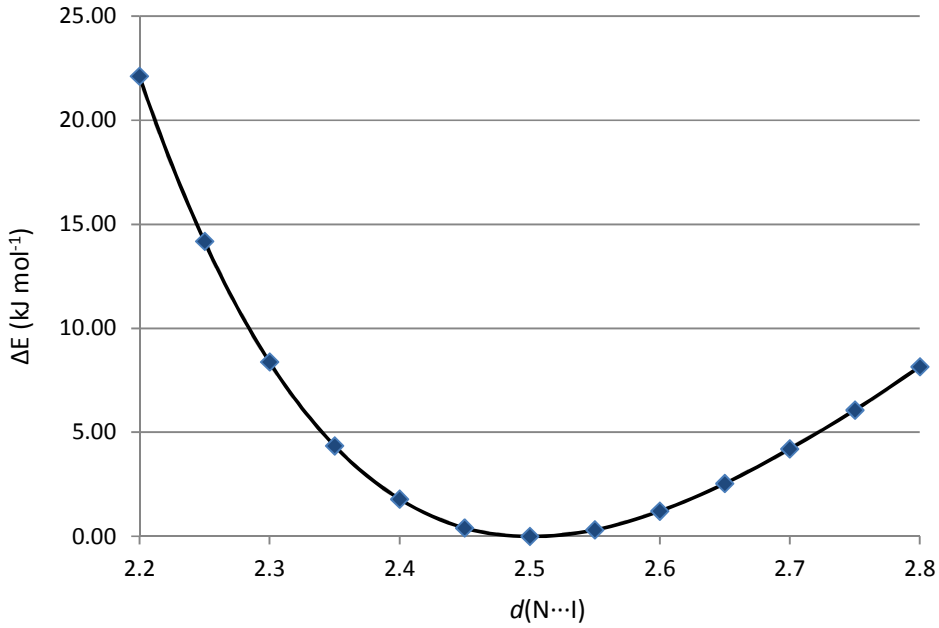

Fig. S7. Potential energy surface scan (M05-2X/def2-TZVPP) along the N···I_2 bond.

Table S3. Optimized geometrical parameters derived from theoretical calculations.

1a (M05-2x/def2-TZVPP)

I	0.000060	0.000000	0.521770
I	0.000060	0.000000	3.272398
N	0.000060	0.000000	-1.978358
N	0.000060	0.000000	-4.519661
C	0.060956	1.383018	-2.470436
H	1.005752	1.806990	-2.138531
H	-0.743146	1.944329	-2.001177
C	-1.228118	-0.638771	-2.470436
H	-2.067686	-0.032540	-2.138531
H	-1.312176	-1.615800	-2.001177
C	-0.060248	1.370588	-4.018540
H	-1.005153	1.804957	-4.337075
H	0.743054	1.944670	-4.473764
C	1.167340	-0.744247	-2.470436
H	1.062113	-1.774451	-2.138531
H	2.055501	-0.328530	-2.001177
C	-1.156751	-0.737522	-4.018540
H	-1.060472	-1.773018	-4.337075
H	-2.055571	-0.328883	-4.473764
C	1.217178	-0.633066	-4.018540

H	2.065804	-0.031938	-4.337075
H	1.312696	-1.615787	-4.473764

1b (M05-2x/def2-TZVPP)

C	-0.068641	1.381072	0.772443
N	0.000000	0.000000	1.262044
C	1.230364	-0.631091	0.772443
C	1.162710	-0.748449	-0.772443
N	0.000000	0.000000	-1.262044
C	0.066821	1.381161	-0.772443
C	-1.161723	-0.749981	0.772443
C	-1.229531	-0.632712	-0.772443
I	0.000000	0.000000	-3.828254
I	0.000000	0.000000	-6.555161
H	2.054004	-0.344280	-1.244646
H	1.050268	-1.781191	-1.092426
H	-1.325157	-1.606680	-1.244646
H	-2.067691	-0.018964	-1.092426
H	1.327273	-1.604932	1.244646
H	2.067714	-0.016239	1.092426
H	-0.728847	1.950960	-1.244646
H	1.017422	1.800154	-1.092426
H	-2.053549	-0.346986	1.244646
H	-1.047920	-1.782573	1.092426
H	0.726276	1.951918	1.244646
H	-1.019794	1.798812	1.092426
I	0.000000	0.000000	3.828254
I	0.000000	0.000000	6.555161

1a (MP2/aug-cc-pVTZ)

I	0.000000	0.000000	0.468590
I	0.000000	0.000000	3.250228
N	0.000000	0.000000	-1.955498
N	0.000000	0.000000	-4.505996
C	0.981242	0.982911	-2.452228
H	1.966421	0.644889	-2.129095
H	0.772560	1.937137	-1.967761
C	-1.341847	0.358325	-2.452228
H	-1.541700	1.380526	-2.129095
H	-2.063889	-0.299512	-1.967761
C	0.865540	1.066744	-3.996904
H	0.434913	2.020526	-4.304104
H	1.845693	0.972376	-4.465068
C	0.360604	-1.341236	-2.452228
H	-0.424721	-2.025415	-2.129095
H	1.291330	-1.637625	-1.967761

C	-1.356598	0.216207	-3.996904
H	-1.967284	-0.633617	-4.304104
H	-1.764949	1.112229	-4.465068
C	0.491058	-1.282952	-3.996904
H	1.532370	-1.386909	-4.304104
H	-0.080744	-2.084605	-4.465068

1b (MP2/aug-cc-pVTZ)

C	-1.231850	0.639095	0.771878
N	0.000000	0.000000	1.263460
C	1.169398	0.747266	0.771878
C	1.231850	0.639095	-0.771878
N	0.000000	0.000000	-1.263460
C	-1.169398	0.747266	-0.771878
C	0.062452	-1.386361	0.771878
C	-0.062453	-1.386361	-0.771878
I	0.000000	0.000000	-3.732202
I	0.000000	0.000000	-6.491618
H	1.314880	1.617849	-1.244151
H	2.071092	0.027678	-1.103628
H	0.743659	-1.947644	-1.244151
H	-1.011576	-1.807457	-1.103628
H	2.058538	0.329794	1.244151
H	1.059516	1.779779	1.103628
H	-2.058538	0.329795	-1.244151
H	-1.059516	1.779779	-1.103628
H	-0.743660	-1.947643	1.244151
H	1.011575	-1.807457	1.103628
H	-1.314879	1.617850	1.244151
H	-2.071092	0.027679	1.103628
I	0.000000	0.000000	3.732202
I	0.000000	0.000000	6.491618

[**2**···I_2]PF_6

C	1.501823	2.947172	6.111013
N	2.319843	2.750987	4.863172
C	3.620309	3.457514	5.048044
C	4.428704	2.706909	6.127101
N	3.540988	1.839679	6.897534
C	2.376338	2.610942	7.332355
C	3.082693	0.734633	6.049601
C	2.607803	1.284794	4.695423
C	1.541668	3.309742	3.700458
C	2.038655	2.903073	2.328555
C	1.148342	3.552883	1.271500
C	1.554106	3.157105	-0.140948

C	0.667740	3.793173	-1.203129
C	1.077657	3.385508	-2.611828
F	-0.116149	0.303694	5.529528
P	-1.324370	0.536065	4.433337
F	-2.401806	0.319521	5.578755
F	-2.443574	0.824370	3.343807
F	-1.294411	-1.013950	4.084017
F	-0.159586	0.805631	3.304819
F	-1.254369	2.130595	4.793561
H	2.268423	0.224833	6.556149
H	3.898210	0.031572	5.906721
H	3.378546	1.211589	3.934499
H	1.701072	0.802711	4.354034
H	2.731867	3.506148	7.836524
H	0.641446	2.295177	6.020210
H	0.521772	2.965036	3.835960
H	1.967301	1.824371	2.214595
H	3.075163	3.201020	2.163796
H	4.908946	3.413374	6.798157
H	5.201768	2.087549	5.680383
H	4.132639	3.477240	4.092686
H	3.383018	4.475121	5.346285
H	1.806140	2.021498	8.043670
H	1.169205	3.980903	6.110025
H	1.573688	4.391366	3.823985
H	1.187075	4.639648	1.370690
H	0.116535	3.248941	1.451456
H	2.593370	3.443852	-0.318689
H	1.506427	2.070843	-0.235712
H	-0.367531	3.504676	-1.020943
H	0.712184	4.878697	-1.104598
H	0.438032	3.845373	-3.360891
H	2.104749	3.684138	-2.816007
H	1.014036	2.305519	-2.731962
I	4.933077	0.964391	8.999424
I	6.395725	0.129543	11.111076

[**3**···I_2]PF_6

C	0.690216	-0.302045	-0.563513
N	0.945272	-0.607471	0.886426
C	0.281819	0.447381	1.730140
C	-1.244140	0.298673	1.596343
N	-1.550772	-0.511566	0.417518
C	-0.803517	0.021118	-0.726160
C	-1.140460	-1.891283	0.665431
C	0.307310	-1.918804	1.199474

C	2.415987	-0.609455	1.212618
C	3.301112	-1.351288	0.232622
C	4.749243	-1.247812	0.706705
C	5.716592	-1.929902	-0.250232
C	7.164135	-1.818200	0.207785
C	8.139017	-2.489496	-0.749258
I	-4.182053	-0.534848	-0.034068
I	-6.846867	-0.626070	-0.465196
F	1.062642	2.680496	-0.361172
P	2.616098	3.196908	-0.173734
F	2.556309	2.611907	1.353066
F	2.084337	4.602235	0.338581
F	4.132551	3.618210	0.040269
F	2.628229	3.684603	-1.686270
F	3.101936	1.703269	-0.659039
H	-0.954655	1.095820	-0.767598
H	-1.188012	-0.419987	-1.641250
H	0.976077	-1.191527	-1.116274
H	1.321377	0.530443	-0.845859
H	-1.683288	-0.186635	2.464460
H	0.642257	1.402404	1.367269
H	2.709677	0.434372	1.250836
H	3.233310	-0.890023	-0.749354
H	3.021297	-2.401919	0.142399
H	-1.817059	-2.341246	1.386380
H	-1.226892	-2.442140	-0.267261
H	0.899336	-2.700972	0.737459
H	0.344579	-2.034324	2.279327
H	-1.701850	1.276550	1.483308
H	0.626377	0.298462	2.749102
H	2.490299	-1.039075	2.210659
H	4.847092	-1.689686	1.700460
H	5.010579	-0.192706	0.795370
H	5.449202	-2.984161	-0.353056
H	5.615920	-1.480759	-1.239726
H	7.426815	-0.763955	0.311300
H	7.266334	-2.264080	1.199639
C	9.587714	-2.376346	-0.294271
H	7.875972	-3.544561	-0.855498
H	8.037136	-2.042777	-1.740531
C	10.551510	-3.050710	-1.261426
H	9.847079	-1.322308	-0.189382
H	9.687155	-2.821260	0.696799
H	11.581788	-2.962789	-0.925184
H	10.318328	-4.109717	-1.360678
H	10.480313	-2.600598	-2.250176

[**4**···I_2]PF_6

C	0.077912	-0.146279	-0.476077
N	0.315131	-0.349200	0.994802
C	-0.450308	0.695929	1.760503
C	-1.956459	0.422779	1.597905
N	-2.166768	-0.475343	0.462473
C	-1.431111	0.047626	-0.693029
C	-1.659178	-1.802360	0.801205
C	-0.228814	-1.686640	1.368900
C	1.772591	-0.219396	1.354029
C	2.735958	-0.943553	0.436500
C	4.160147	-0.709894	0.935877
C	5.196592	-1.370562	0.038026
C	6.621582	-1.131062	0.517062
C	7.662270	-1.782430	-0.383094
I	-4.769992	-0.738475	-0.060206
I	-7.402697	-1.073998	-0.562867
F	0.212978	2.864284	-0.435058
P	1.716973	3.508408	-0.240326
F	1.658712	3.005509	1.315596
F	1.066359	4.894625	0.178218
F	3.190614	4.056454	-0.014442
F	1.735039	3.911459	-1.777446
F	2.327900	2.032098	-0.627729
H	-1.663919	1.102747	-0.802283
H	-1.754500	-0.474823	-1.588723
H	0.448298	-1.039505	-0.969411
H	0.650027	0.716747	-0.790756
H	-2.383034	-0.043828	2.482365
H	-0.152785	1.654777	1.353435
H	1.985596	0.844465	1.340193
H	2.660836	-0.540396	-0.570224
H	2.535614	-2.015288	0.396521
H	-2.319070	-2.261270	1.531960
H	-1.677651	-2.411034	-0.098772
H	0.433803	-2.445007	0.967084
H	-0.212503	-1.737778	2.454202
H	-2.482876	1.354470	1.415268
H	-0.125157	0.629739	2.794487
H	1.852607	-0.587473	2.375937
H	4.264027	-1.090171	1.954170
H	4.343480	0.364554	0.972178
H	5.006994	-2.445339	-0.011820
H	5.087907	-0.983811	-0.976668
H	6.807270	-0.056744	0.566630

H	6.732098	-1.514091	1.533929
C	9.088849	-1.540690	0.090259
H	7.475907	-2.857598	-0.433960
H	7.549731	-1.399184	-1.399310
C	10.130162	-2.190361	-0.810093
H	9.274497	-0.465852	0.140096
H	9.202084	-1.922315	1.107385
C	11.557727	-1.947764	-0.339299
H	9.945431	-3.265913	-0.860495
H	10.016925	-1.809119	-1.827344
C	12.586863	-2.603919	-1.250118
H	11.739665	-0.873449	-0.290430
H	11.668382	-2.327976	0.677171
H	13.601505	-2.423173	-0.903277
H	12.431595	-3.680886	-1.291821
H	12.503509	-2.217096	-2.264458

4-picoline···I_2

C	0.001278	0.013693	0.005323
N	0.002840	0.001703	1.332630
C	1.166986	-0.011468	1.970551
C	2.377928	-0.011686	1.304183
C	2.393174	0.003907	-0.085246
C	1.166773	0.014494	-0.737985
C	3.682348	0.033423	-0.848827
I	-2.228686	-0.002065	2.645521
I	-4.572822	-0.005324	4.021159
H	1.120627	-0.024770	3.049876
H	3.299841	-0.027331	1.864743
H	1.116832	0.019980	-1.815856
H	-0.968199	0.020306	-0.471517
H	3.567236	-0.427205	-1.825545
H	4.000293	1.064102	-0.999284
H	4.468407	-0.482356	-0.305044

1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)···I_2

C	-7.512691	6.108544	-0.055755
N	-6.399491	5.187171	-0.218129
C	-6.775684	3.891338	-0.173730
C	-8.272657	3.818856	-0.044460
C	-8.724497	5.239116	-0.403796
C	-5.013969	5.596533	-0.086204
C	-4.197789	4.430225	0.453361
C	-4.557564	3.155201	-0.299815
N	-5.985062	2.885481	-0.215619
H	-4.268615	3.241632	-1.349075

H	-4.029623	2.300866	0.114405
H	-3.137193	4.645963	0.357451
H	-4.421544	4.287484	1.509349
H	-4.629963	5.923081	-1.052900
H	-4.970647	6.446020	0.594146
H	-7.553380	6.476419	0.972191
H	-7.401658	6.961857	-0.720408
H	-9.617908	5.547309	0.127245
H	-8.919792	5.303247	-1.470751
H	-8.509270	3.560756	0.987114
H	-8.686375	3.044721	-0.680319
I	-6.730850	0.577609	0.022965
I	-7.522090	-2.057934	0.325262

$NH_3\cdots I_2$

N	0.031122	-0.053905	0.022008
C	0.006285	-0.010885	1.477712
C	1.395294	-0.010885	-0.486642
C	-0.688220	-1.213802	-0.486642
H	-0.693722	-1.185167	-1.572342
H	-0.214471	-2.141799	-0.151652
H	-1.713664	-1.185167	-0.129932
H	-1.024674	0.008199	1.818825
H	0.511048	-0.885161	1.900427
H	0.505237	0.891494	1.818825
H	1.373247	0.008198	-1.572346
H	1.883217	0.891494	-0.129931
H	1.962089	-0.885161	-0.151653
I	-1.163686	2.015564	-0.822850
I	-2.457129	4.255872	-1.737452

DABCO, in C_3-symmetry (minimum)

N	0.000000	0.000000	1.281084
N	0.000000	0.000000	-1.283022
C	0.879852	1.054138	0.774321
H	1.895172	0.821928	1.094580
H	0.594102	1.997313	1.238598
C	-1.352836	0.234905	0.774321
H	-1.659396	1.230303	1.094580
H	-2.026775	-0.484149	1.238598
C	0.781016	1.130220	-0.774991
H	0.286412	2.046657	-1.096128
H	1.766190	1.105930	-1.238892
C	0.472984	-1.289043	0.774321
H	-0.235775	-2.052231	1.094580
H	1.432673	-1.513164	1.238598

C	-1.369307	0.111270	-0.774991
H	-1.915663	-0.775289	-1.096128
H	-1.840859	0.976601	-1.238892
C	0.588291	-1.241489	-0.774991
H	1.629251	-1.271369	-1.096128
H	0.074669	-2.082531	-1.238892

DABCO, in D_{3h}-symmetry (1 imaginary frequency)

N	0.000000	0.000000	1.280786
N	0.000000	0.000000	-1.280786
C	-1.189835	-0.686951	0.777446
H	-2.067379	-0.177973	1.174375
H	-1.187819	-1.701416	1.174375
C	1.189835	-0.686951	0.777446
H	1.187819	-1.701416	1.174375
H	2.067379	-0.177973	1.174375
C	-1.189835	-0.686951	-0.777446
H	-1.187819	-1.701416	-1.174375
H	-2.067379	-0.177973	-1.174375
C	0.000000	1.373903	0.777446
H	0.879560	1.879389	1.174375
H	-0.879560	1.879389	1.174375
C	1.189835	-0.686951	-0.777446
H	2.067379	-0.177973	-1.174375
H	1.187819	-1.701416	-1.174375
C	0.000000	1.373903	-0.777446
H	-0.879560	1.879389	-1.174375
H	0.879560	1.879389	-1.174375

Table S4. List of DFT functionals trialed for use in calculations.

	d(N···I)/Å	*d*(I–I)/Å
B3LYP	2.632	2.793
B97D	2.618	2.832
BP86	2.584	2.811
BVP86	2.583	2.810
PBE0	2.555	2.753
PBE-D	2.564	2.803

All optimizations reported here resulted in C_{3v} symmetric geometries found as minima by vibrational analysis.

Table S5. Results from natural decomposition analysis (NEDA).

	1a	**1b**	[**2**···I_2]PF_6	[**3**···I_2]PF_6	[**4**···I_2]PF_6
CT	-233.5	-191.9	-135.1	-134.6	-135.3
ES	-166.7	-139.9	-96.8	-96.5	-96.9
POL	-153.7	-131.8	-107.0	-106.8	-107.2
XC	-104.1	-90.5	-71.6	-71.4	-71.7
DEF(A)	196.8	164.5	120.2	119.8	120.3
DEF(B)	401.5	338.3	257.7	256.9	258.0
SE(A)	3.3	1.9	3.8	3.7	3.7
SE(B)	75.9	65.0	50.3	50.2	50.4
Electrical(ES +POL+SE)	-241.3	-204.7	-149.8	-149.4	-150.0
CORE (XC+DEF-SE)	415.1	345.4	252.2	251.4	252.6
ΔE_{int}	-59.7	-51.2	-32.6	-32.6	-32.6