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ELECTRONIC SUPPORTING INFORMATION

A PGSE NMR Approach to the Characterization of Single and Multi-Site Halogen-Bonded Adducts in Solution

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Equations for 1:1 adducts

For 1:1 adducts, the value of the association constant between a XB donor (D) and an XB acceptor (A) (K_a) can be estimated according to the Eq. S1 and S2:[1]

$$V_H(D) = \alpha V_H^0(D) + (1-\alpha)V_H^{agg}(D,A) \qquad \text{Eq.S1}$$

$$K_a = \frac{(1-\alpha)c(D)}{\alpha c(D)\times[c(A)-(1-\alpha)c(D)]} \qquad \text{Eq.S2}$$

Where V_H(D) is the experimentally measured volume of D, V_H^0(D) is its volume in absence of any aggregation process, α is the molar fraction of free D and V_H^{agg}(D,A) is the volume of the aggregate between the two species. Generally, V_H^{agg}(D,A) is taken as the sum of V_H^0(D) and V_H^0(A). Clearly, similar equations can be derived if V_H(A) is measured instead of V_H(D).

^{19}F NMR Titrations.

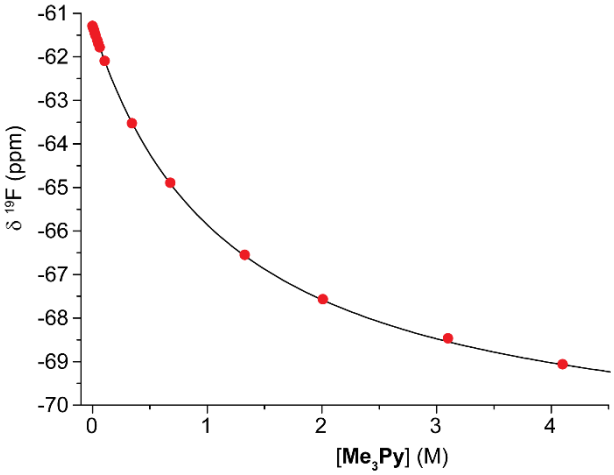

Figure S1. Trend of the chemical shift of the α-fluorine nuclei (-CF_2I) of **I1** (*C* = 24 mM) with [**Me$_3$Py**]. The limit value of δ (fitted) is -71.36 ± 0.04 ppm, the value of K_a is 0.85 ± 0.01 M^{-1}.

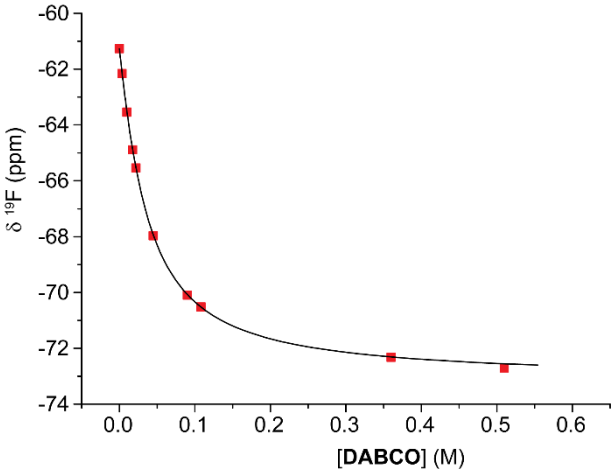

Figure S2. Trend of the chemical shift of the α-fluorine nuclei (-CF_2I) of **I1** (*C* = 20 mM) with [**DABCO**]. The limit value of δ (fitted) is -73.25 ± 0.03 ppm, the value of K_a is 37.2 ± 0.4 M^{-1}.

Equations for 1:2 adducts

For systems containing both 1:1 and 1:2 adducts (one acceptor and two donor moieties), the concentration of free D has been calculated with the equation S3:[2]

$$[D]^3*B1 + [D]^2*B2 + [D]*B3 - C_0(D) \qquad \text{Eq.S3}$$

with

$B1 = K_{a1} * K_{a2}$

$B2 = K_{a1} *[2K_{a2}*C_0(A)- K_{a2}*C_0(D)+1]$

$B3 = K_{a1} *[C_0(A)- C_0(D)]+1$

The resulting data ([D]; $V_H(A)$) has been fitted with the equation S4

$$V_H(A) = (V_H^0(A) + V_H^0(A,D)*K_{a1}*[D] + V_H^0(A,2D)*K_{a1}*K_{a2}*[D]^2)/(1+K_{a1}*[D]+ K_{a1}*K_{a2}*[D]^2) \qquad \text{Eq.S4}$$

PGSE Studies

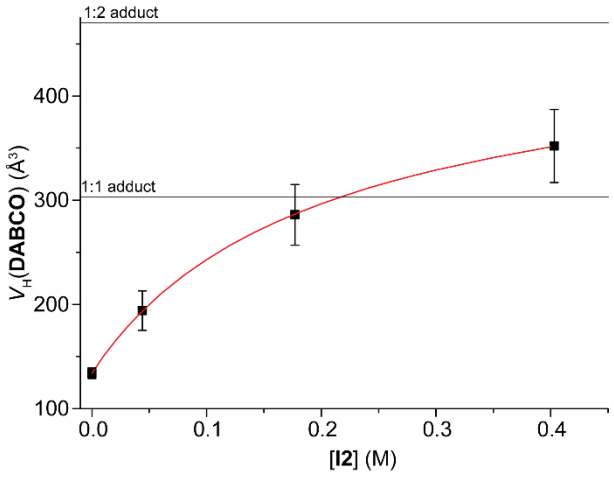

Figure S3. Experimental hydrodynamic volume of **DABCO** (*C* = 8.8 mM) at different concentrations of **I2**. The solid red line represents the best fit. K_{a1} = 11.0 ± 0.2 and K_{a2} = 2.1 ± 0.1 M^{-1}.

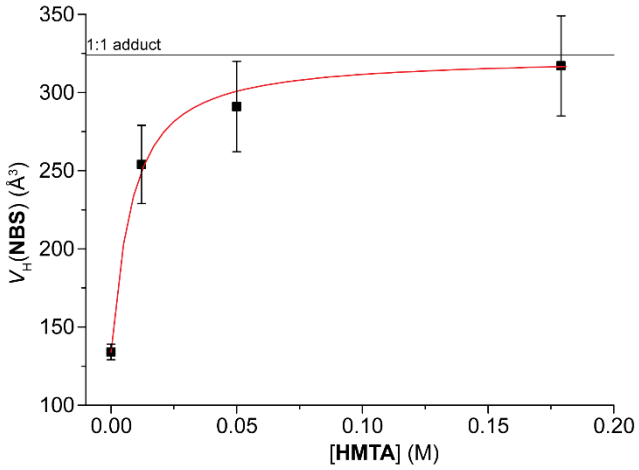

Figure S4. Experimental hydrodynamic volume of **NBS** (*C* = 3.9 mM) at different concentrations of **HMTA**. The solid red line represents the best fit. K_{a1} = 161 ± 27 M^{-1}.

DFT Calculations

Table S1. Thermodynamic values (in kcal/mol) for the different adducts with respect to the isolated components (T = 298 K).

	ΔE	**ΔH**	**ΔS**	**ΔG**
		Gas-phase		
hmta-nbs	-10.2	-8.7	-33.9	1.4
hmta-2nbs	-19.2	-15.8	-72.3	5.7
hmta-3nbs	-26.8	-24.4	-123.7	12.4
		Solvent = Chloroform		
hmta-nbs	-11.6	-8.6	-43.3	4.3
hmta-2nbs	-20.5	-15.1	-75.3	7.3
hmta-3nbs	-28.0	-24.0	-128.7	14.3

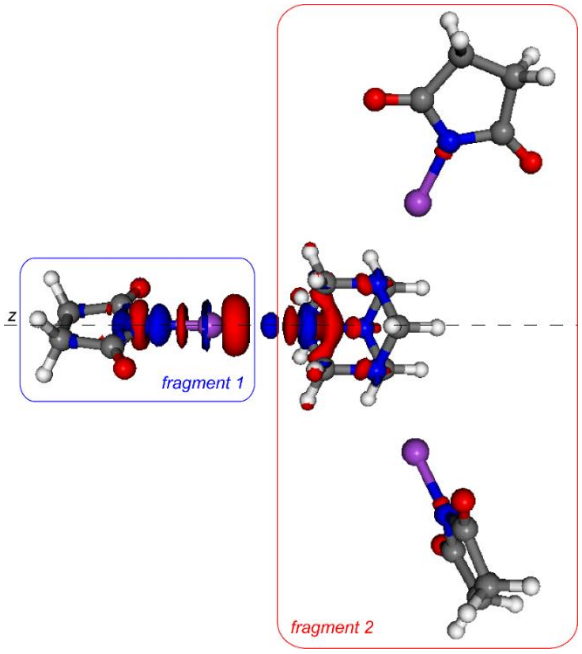

Figure S5. 3D contour plot of the change of electronic density upon formation of the adduct **HMTA/NBS** (1:2). Blue (red) isosurfaces identify regions in which the electron density increases (decreases). Density value at the isosurfaces: ±0.001 au

hmta

22

N	-0.225450	0.209732	0.805324
C	0.281224	-1.148763	1.016255
H	1.370530	-1.137199	0.929686
H	0.016630	-1.472031	2.026003
C	0.120963	0.609126	-0.561732
H	1.209291	0.633096	-0.657273
H	-0.266009	1.614733	-0.744135
C	-1.686588	0.161484	0.900240
H	-1.964711	-0.154735	1.908649
H	-2.085253	1.164404	0.728738
N	-0.259576	-2.112653	0.053033
N	-2.288761	-0.760093	-0.067821
N	-0.423735	-0.299366	-1.575001
C	-1.879406	-0.331558	-1.408229
H	-2.304189	-1.019487	-2.143401
H	-2.278783	0.668029	-1.596703
C	-1.720363	-2.089786	0.169284
H	-2.143124	-2.788992	-0.556481
H	-2.000306	-2.420274	1.172621
C	0.088345	-1.643229	-1.291207
H	1.176413	-1.634602	-1.391988
H	-0.323143	-2.339838	-2.025866

nbs

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Br	0.729002	4.717195	20.422614
N	0.112583	5.752173	21.816432
C	0.751268	6.934901	22.206479
O	1.734359	7.393730	21.699469
C	-0.051650	7.477070	23.366306
H	-0.382806	8.483482	23.113681
H	0.611304	7.579128	24.224482
C	-1.193744	6.495857	23.589777
H	-1.187088	6.034467	24.576415
H	-2.181173	6.938415	23.465264
C	-1.025721	5.407918	22.554417
O	-1.704769	4.438374	22.372929

hmta-nbs

34

Br	0.0000	-0.0000	-2.5332
N	-0.0020	-0.0263	-4.4407
C	1.1599	0.1027	-5.1914
O	2.2683	0.2485	-4.7487
C	0.7518	0.0224	-6.6483
H	1.2953	-0.7985	-7.1146
H	1.0804	0.9313	-7.1508
C	-0.7566	-0.1654	-6.6441
H	-1.3007	0.6356	-7.1429
H	-1.0851	-1.0941	-7.1093
C	-1.1639	-0.1883	-5.1849
O	-2.2716	-0.3203	-4.7362
N	0.0000	0.0000	0.0000
N	-1.0553	-0.9829	1.9536
C	-1.2884	0.3717	2.4621
H	-2.2667	0.7154	2.1193
H	-1.2911	0.3427	3.5534
N	-0.2660	1.3255	2.0174
C	-0.2640	1.3386	0.5596
H	0.5069	2.0226	0.1983
H	-1.2341	1.6804	0.1924
C	-1.0393	-0.9218	0.4981

H	-2.0094	-0.5786	0.1322
H	-0.8445	-1.9156	0.0893
N	1.3384	-0.5116	1.9585
C	1.0395	0.8301	2.4670
H	1.0487	0.8037	3.5583
H	1.8158	1.5193	2.1280
C	0.2714	-1.4127	2.4054
H	0.4693	-2.4155	2.0207
H	0.2765	-1.4504	3.4965
C	1.3077	-0.4619	0.5034
H	2.0786	0.2205	0.1395
H	1.5030	-1.4559	0.0952

hmta-2nbs

46

Br	0.0000	0.0000	2.5860
N	0.0190	0.0555	4.4777
C	-0.5688	-0.9284	5.2678
O	-1.1452	-1.9011	4.8613
C	-0.3360	-0.5256	6.7082
H	0.1996	-1.3310	7.2090
H	-1.3020	-0.4454	7.2050
C	0.4364	0.7829	6.6543
H	-0.0837	1.6192	7.1192
H	1.4176	0.7330	7.1244
C	0.6238	1.0915	5.1845
O	1.1805	2.0383	4.6975
Br	3.7331	-0.4046	-2.9609
N	5.4859	-0.5364	-3.6652
C	6.6185	-0.2662	-2.9023
O	6.6218	0.0651	-1.7476
C	7.8126	-0.4702	-3.8099
H	8.4627	-1.2207	-3.3622
H	8.3867	0.4550	-3.8383
C	7.2427	-0.8794	-5.1595
H	7.4885	-0.1907	-5.9666
H	7.5636	-1.8661	-5.4906

C	5.7389	-0.8966	-4.9849
O	4.9067	-1.1644	-5.8094
N	-0.9398	-0.9754	-2.0164
C	-1.3839	0.3640	-2.4160
H	-1.4060	0.4186	-3.5056
H	-2.3930	0.5298	-2.0354
N	-0.5037	1.4205	-1.9049
N	0.0000	0.0000	0.0000
C	0.8422	1.1751	-2.4079
H	1.5236	1.9362	-2.0228
H	0.8417	1.2258	-3.4981
N	1.3455	-0.1518	-2.0035
C	0.4156	-1.1743	-2.5186
H	0.4139	-1.1217	-3.6088
H	0.7790	-2.1586	-2.2166
C	-0.4714	1.3235	-0.4507
H	-1.4734	1.4874	-0.0501
H	0.1956	2.0863	-0.0445
C	-0.8999	-1.0259	-0.5585
H	-0.5520	-2.0084	-0.2333
H	-1.9022	-0.8611	-0.1594
C	1.3469	-0.2198	-0.5380
H	2.0228	0.5405	-0.1420
H	1.7042	-1.2024	-0.2237

hmta-3nbs

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Br	0.0000	0.0000	-2.6277
N	0.0212	-0.0338	-4.5101
C	-1.0825	0.3305	-5.2779
O	-2.1394	0.7053	-4.8485
C	-0.6782	0.1547	-6.7252
H	-0.7917	1.1113	-7.2336
H	-1.3816	-0.5291	-7.1987
C	0.7532	-0.3589	-6.6997
H	0.8739	-1.3417	-7.1539
H	1.4650	0.2978	-7.1980
C	1.1315	-0.4580	-5.2376
O	2.1721	-0.8316	-4.7686
N	0.0000	0.0000	0.0000
Br	1.4036	3.4825	2.9813
N	2.0047	5.1327	3.6640
C	2.3880	6.1907	2.8416
O	2.3841	6.1788	1.6407
C	2.7884	7.3262	3.7570
H	2.1710	8.1926	3.5234
H	3.8143	7.6097	3.5258
C	2.6020	6.8051	5.1738
H	3.5210	6.7855	5.7580

H	1.8797	7.3732	5.7585
C	2.0927	5.3876	5.0309
O	1.8200	4.6112	5.9058
N	-1.3171	-0.3435	2.0005
C	-0.3881	-1.4214	2.3971
H	-0.3701	-1.4780	3.4866
H	-0.7668	-2.3658	2.0036
N	0.9614	-1.1837	1.8941
C	1.4294	0.0937	2.4211
H	2.4332	0.2999	2.0468
H	1.4657	0.0481	3.5108
N	0.5437	1.2034	2.0238
C	-0.8048	0.9255	2.5300
H	-0.7766	0.8737	3.6198
H	-1.4755	1.7347	2.2356
C	0.8991	-1.0842	0.4396
H	0.5345	-2.0252	0.0248
H	1.8956	-0.8910	0.0386
C	-1.3398	-0.2626	0.5374
H	-2.0162	0.5371	0.2297
H	-1.7105	-1.2064	0.1337
C	0.4901	1.2652	0.5598
H	1.4900	1.4661	0.1712
H	-0.1718	2.0780	0.2556
Br	-3.6804	-0.9125	2.9703

N	-5.3580	-1.3758	3.6929
C	-6.3626	-0.4418	3.9308
C	-5.6787	-2.6869	4.0317
C	-7.0941	-2.6615	4.5683
H	-7.0850	-3.0636	5.5804
H	-7.7025	-3.3429	3.9749
O	-6.2853	0.7388	3.7224
O	-4.9497	-3.6358	3.9220
C	-7.5405	-1.2094	4.4927
H	-7.8052	-0.7793	5.4578
H	-8.3981	-1.0466	3.8414

[1] G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia and A. Macchioni, *Organometallics*, 2007, **26**, 3624.
[2] P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305.