Chemistry–A European Journal

Supporting Information

Halogen Bonding Propensity in Solution: Direct Observation and Computational Prediction

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Table S1. Listing of total energies (hartrees) for all XB bond donors, acceptors, and complexes at B3LYP/6-311G** level of theory using Spartan '16.

Donors	**Total Energies (hartrees)**
iodobenzene	-7151.223106
2,6-difluoroiodobenzene	-7349.745974
p-nitroiodobenzene	-7355.777159
iodopentafluorobenzene	-7647.501169
1-iodo-3,5-dinitrobenzene	-7560.324533
Acceptors	
3-nitropyridine	-452.899217
3-fluoropyridine	-347.608788
pyridine	-248.346868
4-dimethylaminopyridine	-382.353830
XB Donor/Acceptor Complex	
iodobenzene/3-nitropyridine	-7604.122323
iodobenzene/3-fluoropyridine	-7498.831894
iodobenzene/pyridine	-7399.569974
iodobenzene/4-dimethylaminopyridine	-7533.576936
2,6-difluoroiodobenzene/3-nitropyridine	-7802.645191
2,6-difluoroiodobenzene/3-fluoropyridine	-7697.354762
2,6-difluoroiodobenzene/pyridine	-7598.092842
2,6-difluoroiodobenzene/4-dimethylaminopyridine	-7732.099804
p-nitroiodobenzene/3-nitropyridine	-7808.676376
p-nitroiodobenzene/3-fluoropyridine	-7703.385947
p-nitroiodobenzene/pyridine	-7604.124027
p-nitroiodobenzene/4-dimethylaminopyridine	-7738.130989
iodopentafluorobenzene/3-nitropyridine	-8100.400386
iodopentafluorobenzene/3-fluoropyrindine	-7995.109957
iodopentafluorobenzene/pyridine	-7895.848037
iodopentafluorobenzene/4-dimethylpyridine	-8029.854999
1-iodo-3,5-dinitrobenzene/3-nitropyridine	-8013.223750
1-iodo-3,5-dinitrobenzene/3-fluoropyridine	-7907.933321
1-iodo-3,5-dinitrobenzene/pyridine	-7808.671401
1-iodo-3,5-dinitrobenzene/4-dimethylpyridine	-7942.678363

Table S2: Calculated theoretical binding energies (ΔE_{bind}) of all XB donor/acceptor complexes (kcal mol^{-1}) at B3LYP-D3/6-311G** level of theory using Spartan '18.

	XB Donors				
XB Acceptors	IB	DFIB	p-NIB	IPFB	IDNB
3-NPy	-4.95	-6.90	-5.76	-8.08	-6.93
3-FPy	-5.16	-7.47	-6.55	-8.67	-7.94
PY	-5.53	-8.08	-7.14	-9.93	-8.75
DMAP	-6.36	-8.87	-8.40	-11.78	-10.85

Table S3: Calculated theoretical binding energies (ΔE_{bind}) for the solvent model (DCM) of all the XB donor/acceptor complexes (kcal mol^{-1}) at B3LYP/6-311G** level of theory using Spartan '18

	XB Donors				
XB Acceptors	IB	DFIB	p-NIB	IPFB	IDNB
3-NPy	-1.95	-3.86	-2.47	-4.87	-3.34
3-FPy	-1.99	-4.19	-2.84	-5.10	-3.81
PY	-2.20	-4.64	-3.16	-5.76	-4.27
DMAP	-2.78	-5.22	-3.89	-7.34	-5.38

Table S4. Calculated C-I bond lengths (Å) for all XB donors and donor/acceptor complexes with interaction distances (Å) and bond angles (°) at B3LYP and B3LYP-D3/6-311G** level of theory using Spartan '16 and '18.

XB Donor and Donor/Acceptor Complex	C-I bond length (Å)[a]	C-I bond length (Å)[b]	C-I bond length (Å)[c]	C-I···N distance (Å)[a]	C-I···N distance (Å)[b]	C-I···N distance (Å)[c]	C-I···N bond angle (°)[a]	C-I···N bond angle (°)[b]	C-I···N bond angle (°)[c]
IB	2.138	2.140	2.143						
IB/3-NPy	2.140	2.139	2.146	3.207	3.194	3.172	179.62	178.40	179.59
IB/3-FPy	2.141	2.141	2.149	3.164	3.111	3.137	179.63	178.28	179.90
IB/PY	2.142	2.143	2.149	3.139	3.068	3.125	179.84	177.90	179.90
IB/DMAP	2.144	2.144	2.151	3.078	3.035	3.075	179.87	179.36	179.88
DFIB	2.108	2.112	2.110						
DFIB/3-NPy	2.120	2.120	2.126	3.098	3.089	3.046	179.58	179.04	179.65
DFIB/3-FPy	2.124	2.123	2.130	3.054	3.048	3.006	179.65	179.23	179.13
DFIB/PY	2.126	2.128	2.135	3.017	2.962	2.937	179.87	178.51	179.89
DFIB/DMAP	2.132	2.135	2.146	2.946	2.896	2.842	179.79	178.86	179.88
p-NIB	2.126	2.130	2.129						
p-NIB/3-NPy	2.133	2.132	2.136	3.128	3.080	3.098	179.47	178.21	179.53
p-NIB/3-FPy	2.134	2.132	2.138	3.086	3.043	3.069	179.80	178.60	179.81
p-NIB/PY	2.135	2.134	2.140	3.057	3.011	3.042	179.92	178.72	179.92
p-NIB/DMAP	2.137	2.139	2.143	2.995	2.951	2.982	179.85	179.51	179.98
IPFB	2.105	2.106	2.107						
IPFB/3-NPy	2.122	2.123	2.128	3.021	2.980	2.955	179.50	178.19	179.57
IPFB/3-FPy	2.127	2.130	2.138	2.953	2.899	2.839	179.86	178.25	179.90
IPFB/PY	2.133	2.135	2.146	2.885	2.848	2.798	179.88	178.40	179.95
IPFB/DMAP	2.144	2.147	2.158	2.795	2.768	2.736	179.99	179.06	179.99
IDNB	2.123	2.127	2.125						
IDNB/3-NPy	2.133	2.131	2.136	3.060	3.010	3.024	179.22	177.93	179.21
IDNB/3-FPy	2.135	2.130	2.139	3.015	3.000	2.987	179.84	178.66	179.86
IDNB/PY	2.139	2.133	2.140	2.962	2.952	2.920	179.92	178.76	179.94
IDNB/DMAP	2.145	2.145	2.153	2.861	2.838	2.810	179.70	179.27	179.99

[a] Spartan '16 calculations (B3LYP/6-311G**), [b] Spartan '18 calculations (B3LYP-D3/6-311G**), and [c] Spartan '18 (B3LYP/6-311G** in DCM), respectively.

Table S5. Cartesian coordinates of the computed IPFB and IDNB/acceptor complexes at the B3LYP/6-311G** level of theory in Q-Chem 5.3.2 for ALMO-EDA.

IPFB/3-NPy Complex
0 1
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0 1
H -2.2862038747 0.3023848969 2.2733190345
C -1.3784360155 0.1944638120 2.8584771106
H -2.3552750686 0.4245362032 4.7639751643
C -1.4162437060 0.2640118990 4.2496682186
C -0.2286182882 0.1248536415 4.9562023187
C 0.9309128487 -0.0789282291 4.2208382988
H 1.7983490247 -0.3005188574 2.2625073686
C 0.8911626009 -0.1399047474 2.8317898700
N -0.2535213489 -0.0027023860 2.1620104666
N 2.2253059519 -0.2317297745 4.9194391595
O 3.2165587297 -0.4107055518 4.2283734387
O 2.2130612905 -0.1675896626 6.1397946082
H -0.1805839783 0.1703660424 6.0357346747
--
0 1
C -0.2652971638 -0.0164565854 -2.9805147179
C -0.2641581045 -0.0082280687 -5.7780300455
C -0.4990498990 1.1700739636 -5.0797623675
C -0.0300709253 -1.1906364095 -5.0864671519
C -0.0325832330 -1.1865332509 -3.6965782384
C -0.4976935634 1.1576949841 -3.6900198536
I -0.2637279138 -0.0211568842 -0.8584385292
F -0.7255795333 2.3088113172 -3.0482262821
F 0.1937781034 -2.3413214752 -3.0614096300
F 0.1945301219 -2.3216535240 -5.7618798131
F -0.2636252118 -0.0042166574 -7.1119440977
F -0.7229908435 2.3050853041 -5.7488590045

IPFB/3-FPy Complex

0 1

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0 1

H	-2.0118348499	-0.4519684946	2.6937728917
C	-1.1201771816	-0.2491749324	3.2776117129
H	-2.0817586447	-0.4761575134	5.1900160798
C	-1.1562944095	-0.2629196027	4.6694646959
C	0.0129681427	0.0000217989	5.3760543835
C	1.1562397785	0.2634308257	4.6403169719
H	2.0178046869	0.4719322285	2.6786833115
C	1.1206161084	0.2630818671	3.2522754386
H	0.0497580894	0.0030294349	6.4584774147
N	-0.0064697344	0.0086566013	2.5852260440
F	2.3163741701	0.5213592761	5.2701015313

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0 1

C	-0.0277436144	-0.0116347371	-5.2944936066
C	-0.0216318294	-0.0038036999	-2.4952931384
C	0.2052088822	1.1709374950	-4.6030477011
C	-0.2576870982	-1.1903289217	-4.5954665848
C	-0.2524448833	-1.1775938335	-3.2056534308
C	0.2060249985	1.1660057687	-3.2131240279
I	-0.0182903711	0.0016821891	-0.3680260844
F	-0.4763249059	-2.3306541851	-2.5647936796
F	0.4319115493	2.3226351013	-2.5796187626
F	-0.4814747598	-2.3261752532	-5.2643271676
F	-0.0307133459	-0.0154219625	-6.6290318905
F	0.4259392223	2.3030605494	-5.2791244017

IPFB/PY Complex

0 1

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0 1

H	-1.9191074	-0.7331105	2.6677156
C	-1.0641895	-0.4063393	3.2517841
H	-1.9907514	-0.7632359	5.1589220
C	-1.1016280	-0.4220865	4.6429048
C	0.0216650	0.0075758	5.3432567
C	1.1352072	0.4344783	4.6258533
H	1.9255264	0.7376683	2.6385034
C	1.0786131	0.4134022	3.2354993
N	0.0024548	0.0022996	2.5573272
H	0.0291459	0.0097210	6.4272519
H	2.0313537	0.7775925	5.1282525

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0 1

C	-0.0101254	-0.0036274	-2.4610035
C	-0.0146264	-0.0060774	-5.2603337
C	0.2075018	1.1771623	-4.5666016
C	-0.2345534	-1.1880952	-4.5638381
C	-0.2299828	-1.1773408	-3.1740170
C	0.2073752	1.1688496	-3.1767365
I	-0.0072071	-0.0021271	-0.3275951
F	0.4234033	2.3264781	-2.5402918
F	-0.4442619	-2.3337927	-2.5348372
F	-0.4485238	-2.3246036	-5.2356278
F	-0.0167210	-0.0072838	-6.5953549
F	0.4194317	2.3124923	-5.2410336

IPFB/DMAP Complex

0 1

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0 1

H	-1.4615043	-1.4467211	0.6671139
C	-0.8077534	-0.7991911	1.2443079
H	-1.5365448	-1.5212564	3.1073454
C	-0.8489941	-0.8399624	2.6264680
C	0.0028632	0.0045587	3.3761937
H	1.5414670	1.5300645	3.1013033
C	0.8532595	0.8475615	2.6230979
H	1.4621680	1.4500624	0.6613097
C	0.8095595	0.8037069	1.2411141
N	0.0041306	0.0060965	4.7435401
C	0.8979829	0.8933906	5.4735489
H	0.6982047	1.9469475	5.2467552
H	1.9497927	0.6871807	5.2447493
H	0.7516481	0.7462939	6.5418729
C	-0.8893486	-0.8785377	5.4772191
H	-0.7401600	-0.7299325	6.5449435
H	-0.6915109	-1.9326829	5.2516597
H	-1.9414994	-0.6713278	5.2507100
N	0.0002992	0.0014543	0.5382605

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0 1

C	-0.0056633	-0.0114883	-7.2023568
C	-0.0033905	-0.0046248	-4.4001546
C	-1.2077207	-0.0048251	-6.5053830
C	1.1975193	-0.0145941	-6.5072930
C	1.1876287	-0.0111320	-5.1174601
C	-1.1955726	-0.0014478	-5.1155775
I	-0.0018818	-0.0017154	-2.2562640
F	-2.3745221	0.0044625	-4.4792240
F	2.3675829	-0.0141900	-4.4829578

F	2.3544308	-0.0214964	-7.1801099
F	-0.0067488	-0.0149794	-8.5383806
F	-2.3657218	-0.0016749	-7.1763518

IDNB/3-NPy Complex

0 1

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0 1

H	2.1745615	-0.7411456	3.1613287
C	1.2936868	-0.4761815	3.7375379
H	2.1813936	-0.9259300	5.6476095
C	1.2974637	-0.5795703	5.1273224
C	0.1477308	-0.2313947	5.8243950
C	-0.9411791	0.2027788	5.0809324
H	-1.7246793	0.6181952	3.1197846
N	0.2368755	-0.0571193	3.0321277
H	0.0764749	-0.2872610	6.9021725
N	-2.1926093	0.5859875	5.7694983
O	-3.1204439	0.9685627	5.0730838
O	-2.2111187	0.4929413	6.9878122
C	-0.8708268	0.2801150	3.6937445

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0 1

C	0.2218384	0.0144435	-4.9750301
C	0.2384515	0.0001957	-2.1613017
C	0.4738401	-1.1430222	-4.2547577
C	-0.0212212	1.1646335	-4.2401680
C	-0.0202885	1.1849127	-2.8496757
C	0.4889294	-1.1773491	-2.8645918
I	0.2487823	-0.0102647	-0.0279573
H	-0.2202556	2.1151780	-2.3371093
H	0.2151495	0.0200187	-6.0543365
H	0.6935959	-2.1129693	-2.3639063
N	-0.2940694	2.4299207	-4.9711151
O	-0.5273851	3.4242307	-4.3011324
O	-0.2656934	2.3879541	-6.1907321
N	0.7399904	-2.4003929	-5.0013628
O	0.6896314	-2.3483287	-6.2198282

O	0.9913743	-3.3991387	-4.3443446

IDNB/3-FPy

0 1

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0 1

H	0.4748705	-2.0089259	3.5712417
C	0.2623094	-1.1176694	4.1523528
H	0.5041506	-2.0726707	6.0667278
C	0.2786431	-1.1510188	5.5444625
C	0.0021128	0.0162128	6.2493054
C	-0.2762784	1.1543471	5.5111285
H	-0.4965166	2.0098621	3.5490851
C	-0.2765994	1.1154534	4.1229983
N	-0.0096015	-0.0092224	3.4566052
H	0.0000211	0.0551983	7.3316760
F	-0.5479552	2.3128079	6.1381678

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0 1

C	0.0081702	-0.0195833	-4.5092539
C	0.0000943	-0.0172292	-1.6933600
C	-1.1679451	0.0992104	-3.7847237
C	1.1801724	-0.1370756	-3.7778881
C	1.2038137	-0.1382201	-2.3874601
C	-1.1996468	0.1028267	-2.3943875
I	-0.0047803	-0.0173139	0.4420494
H	2.1524918	-0.2331528	-1.8785043
H	0.0112441	-0.0205743	-5.5885382
H	-2.1512499	0.1987171	-1.8910969
N	2.4653588	-0.2679124	-4.5125072
O	2.4148249	-0.2716238	-5.7323354
O	3.4846420	-0.3625360	-3.8457371
N	-2.4489402	0.2279095	-4.5270479
O	-3.4722249	0.3219059	-3.8663925
O	-2.3911815	0.2302774	-5.7465679

IDNB/PY Complex

0 1

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0 1

H	-1.9647561	-0.5795081	3.5413072
C	-1.0872542	-0.3201947	4.1260505
H	-2.0440289	-0.5986773	6.0322567
C	-1.1294864	-0.3302915	5.5174398
C	0.0227108	0.0101515	6.2198732
C	1.1680015	0.3459615	5.5041569
H	1.9841905	0.5820863	3.5185389
C	1.1123131	0.3267333	4.1133687
N	0.0091581	0.0011507	3.4319892
H	0.0280167	0.0136880	7.3039209
H	2.0875367	0.6174346	6.0083444

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0 1

C	-0.0149750	-0.0048986	-4.4862692
C	-0.0055202	-0.0031925	-1.6690610
C	0.1271766	1.1671512	-3.7592890
C	-0.1518854	-1.1761250	-3.7569600
C	-0.1500061	-1.2025074	-2.3664974
C	0.1346356	1.1952467	-2.3688654
I	-0.0009230	-0.0019781	0.4696660
H	-0.2610620	-2.1504824	-1.8593926
H	-0.0189423	-0.0055078	-5.5655117
H	0.2489270	2.1438769	-1.8637111
N	-0.3075214	-2.4568584	-4.4939990
O	-0.3125551	-2.4040534	-5.7138975
O	-0.4195340	-3.4759464	-3.8294628
N	0.2775607	2.4470358	-4.4988985
O	0.3947970	3.4668435	-3.8363603
O	0.2734262	2.3928614	-5.7187367

IDNB/DMAP Complex

0 1

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0 1

H	-1.4512180	-1.4552438	1.5586304
C	-0.8013190	-0.8031140	2.1352520
H	-1.5380472	-1.5169420	3.9999052
C	-0.8504746	-0.8367460	3.5178075
C	-0.0041821	0.0133738	4.2671819
H	1.5403378	1.5318052	3.9937924
C	0.8526239	0.8497875	3.5144662
H	1.4722944	1.4410483	1.5529188
C	0.8153117	0.7983043	2.1320965
N	-0.0135550	0.0256760	5.6349042
C	0.8989235	0.8931254	6.3656795
H	0.7363857	1.9478216	6.1178442
H	1.9487142	0.6509528	6.1605068
H	0.7281622	0.7706816	7.4334539
C	-0.8900865	-0.8752120	6.3691703
N	0.0096328	-0.0065868	1.4277682
H	-1.9431842	-0.7017359	6.1219990
H	-0.6596768	-1.9281589	6.1666314
H	-0.7645619	-0.7028713	7.4363370

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0 1

C	-0.0086380	-0.0075077	-6.3989625
C	0.0005041	-0.0041593	-3.5785044
C	-1.1861173	-0.0039610	-5.6665766
C	1.1735046	-0.0096072	-5.6741453
C	1.2045793	-0.0083061	-4.2835802
C	-1.2081251	-0.0020407	-4.2758932
I	0.0064295	0.0005486	-1.4336832
H	-0.0121338	-0.0084749	-7.4780813
H	2.1612965	-0.0103718	-3.7806585

H	-2.1615342	0.0014887	-3.7666996
N	-2.4771462	-0.0014469	-6.4009900
O	-3.5018828	-0.0004089	-5.7353061
O	-2.4284722	-0.0006163	-7.6214733
N	2.4597334	-0.0128936	-6.4169065
O	2.4031771	-0.0146993	-7.6370475
O	3.4887442	-0.0135093	-5.7578373

Table S6: ΔG values (kcal mol^{-1}) of observed XB donor/acceptor complexes were derived from the relative areas of the bound and unbound donors to determine relative concentration of bound and unbound states. These free energy values assume equal Raman scattering intensity for both bound and unbound states of the C-I bond.

	XB Donors		
XB Acceptors	0.50 m DFIB	0.50 m IPFB	0.50 m IDNB
0.75 m 3-FPy		-0.22	
0.75 m PY		-0.51	
0.75 m DMAP	-0.41	-1.78	-2.34

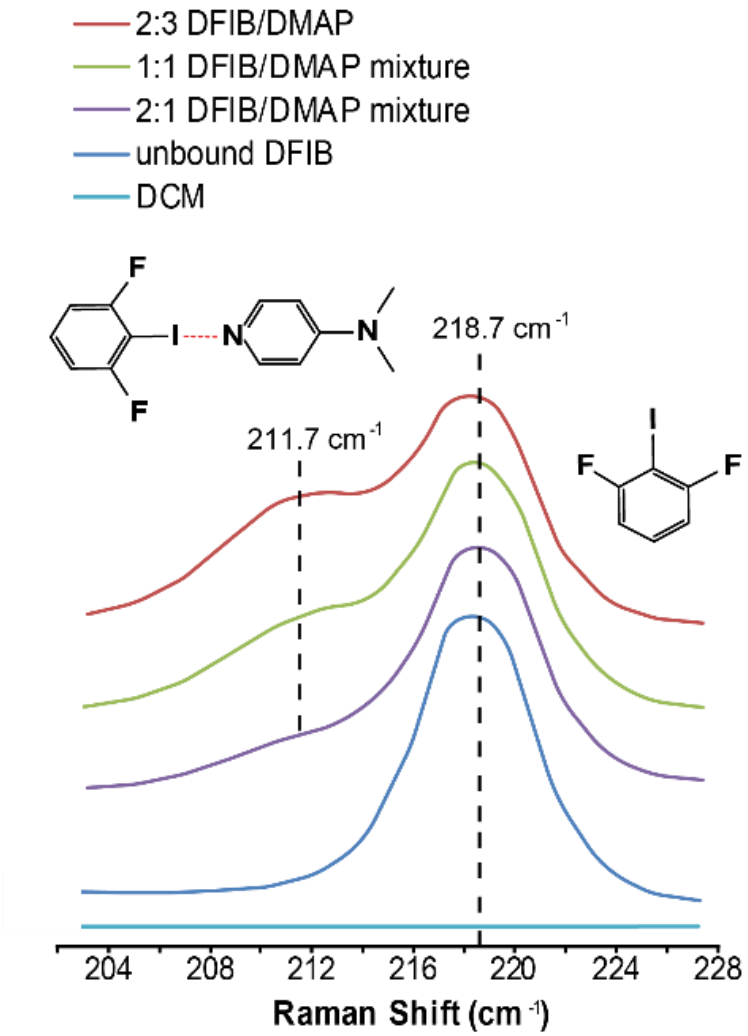

Figure S1. Raman spectra of unbound DFIB and 2:3, 1:1, and 2:1 molar ratios of DFIB/DMAP. solutions.

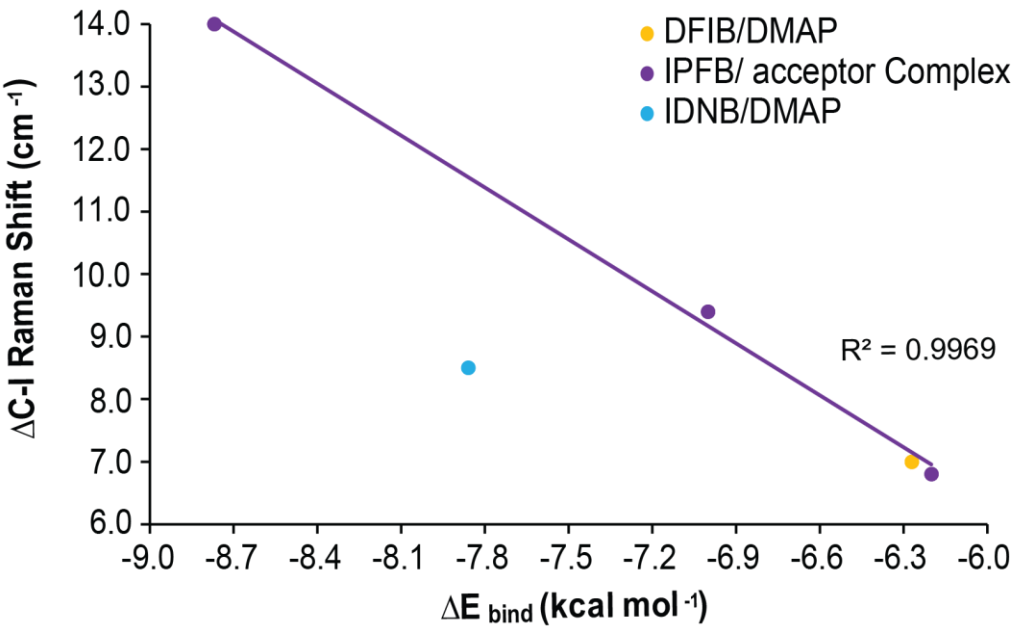

Figure S2. Graph representing the correlation between observed red shifted ΔC-I stretch (cm^{-1}) and ΔE_{bind} (kcal mol^{-1}). The purple line represents the fit for observed IPFB/acceptor complexes.

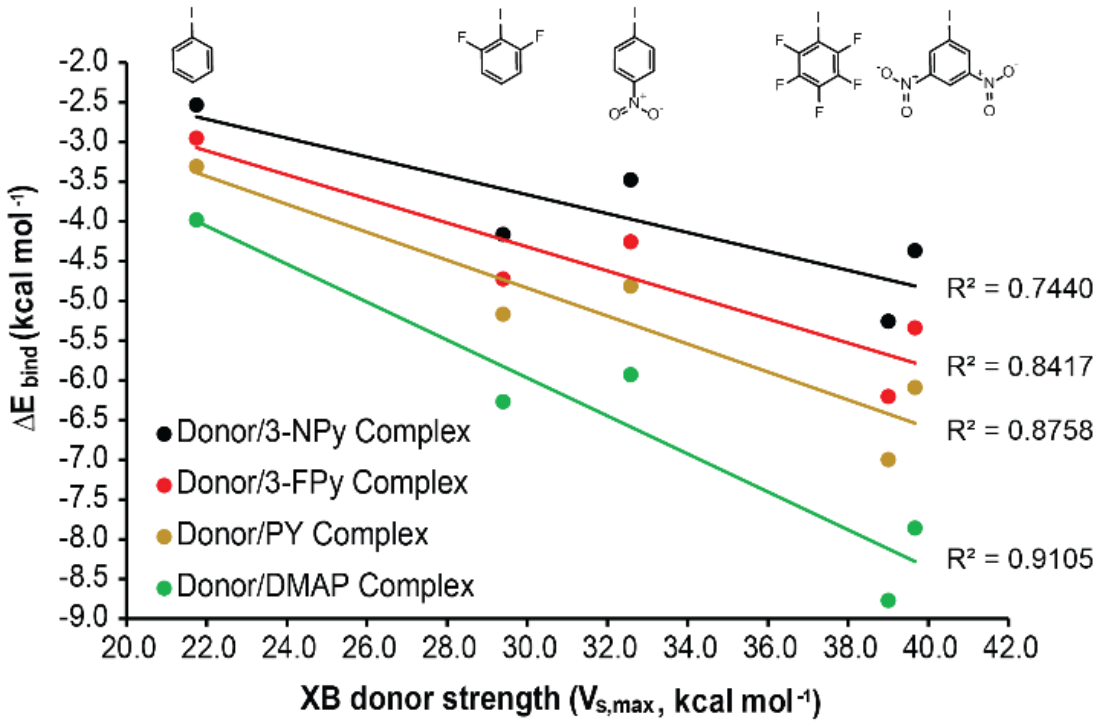

Figure S3. Graph representing the correlation between ΔE_{bind} and XB donor strengths ($V_{s,max}$, kcal mol^{-1}).

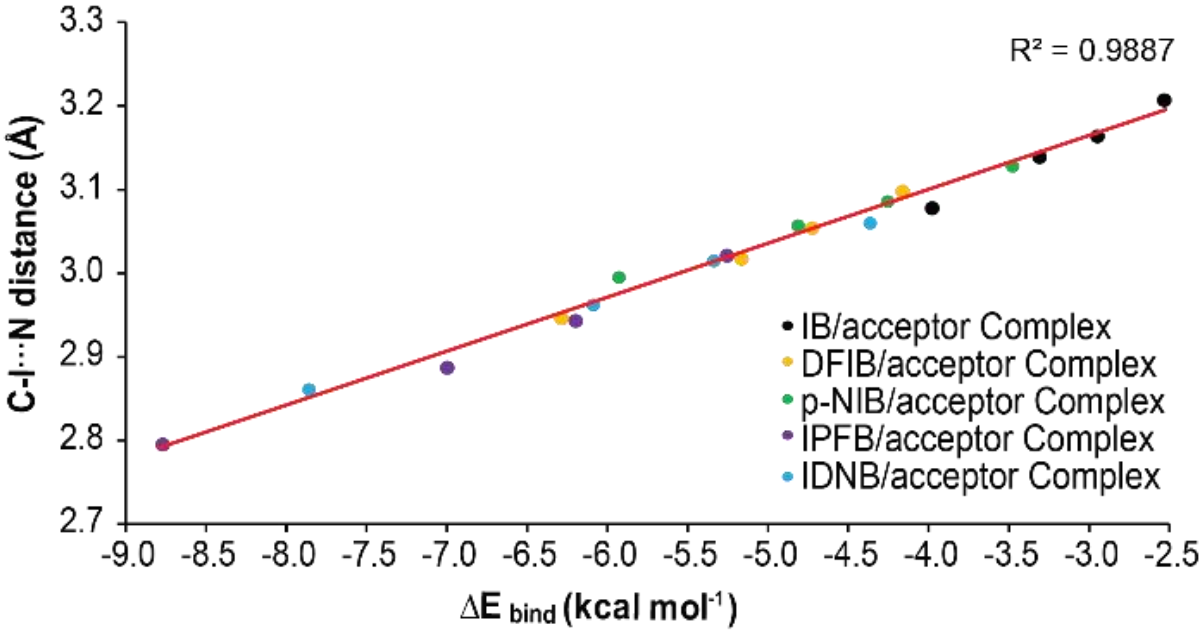

Figure S4. Graph representing the correlation between C-I···N interaction distances (Å) and ΔE_{bind} (kcal mol^{-1}).