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Supporting Information

Supramolecular Hierarchy among Halogen-Bond Donors

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1: Geometry optimization and Molecular Electrostatic Potential Surface calculations

Methods

Geometry optimization was performed using Spartan[1,2] software. The optimization was carried out using DFT with B3LYP procedure and 6-311+G(d,p) as basis set. After the optimization the Electrostatic Potential Surface $V_s(r)$ at a 0.002 IsoValue was calculated using Spartan software.

Atomic coordinates for the modeled compounds

1-iodo-4-(iodoetihinyl)benzene

Coordinates (Angstroms)

ATOM	X	Y	Z
1C	0,000000	0,579191	-1,055066
2 C	0,000000	1,788281	-0,367958
3 C	0,000000	1,784286	1,025561
4 C	0,000000	0,584397	1,735096
5 C	0,000000	-0,621274	1,042923
6 C	0,000000	-0,643166	-0,361731
7 C	0,000000	-1,878475	-1,071316
8 I	0,000000	3,635177	2,095974
9 C	0,000000	-2,923290	-1,681299
10 I	0,000000	-4,631286	-2,715010
11 H	0,000000	0,576591	-2,138345
12 H	0,000000	2,720652	-0,917165
13 H	0,000000	0,584381	2,817112
14 H	0,000000	-1,555466	1,591223

Energy: -14146.303216804 Hartrees

Computed Frequencies (cm^{-1})

58.533, 59.154, 143.725, 147.200, 200.768, 255.041, 277.873, 329.119, 405.551, 408.263 529.185, 530.505, 631.709, 649.037, 711.330, 831.328, 833.353, 834.519, 961.693, 979.483, 014.746, 1067.693, 1128.780, 1205.138, 1251.741, 1297.303, 1324.359, 1416.908, 1508.385, 1581.270, 1619.675, 2266.525, 3188.498, 3189.512, 3204.239, 3209.082

1-iodo-4-(bromoetihinyl)benzene

Coordinates (Angstroms)

ATOM	X	Y	Z
1 C	0,000000	0,000000	1,833634
2 C	0,000000	0,000000	-0,962453
3 C	1,212152	0,000000	1,144245
4 C	-1,212152	0,000000	1,144245
5 C	-1,208656	0,000000	-0,246145
6 C	1,208656	0,000000	-0,246145
7 H	2,152831	0,000000	1,680338
8 H	-2,152831	0,000000	1,680338
9 H	-2,147833	0,000000	-0,785951
10 H	2,147833	0,000000	-0,785951
11 I	0,000000	0,000000	3,964653

Computed frequencies (cm^{-1})

51.397, 58.921, 145.101, 160.267, 211.074, 259.071, 288.382, 345.564, 402.384, 407.11, 527.072, 528.806, 642.803, 649.149, 710.965, 834.455, 836.857, 845.300, 64.153, 981.508, 1013.083, 1067.636, 1131.618, 1207.413, 1256.059, 1296.367, 1327.891, 1418.649, 1510.735, 1581.78, 1620.541, 2285.519, 3186.995, 3187.949, 3201.853, 3203.552

12	C	0,000000	0,000000	-2,387732
13	C	0,000000	0,000000	-3,594998
14	Br	0,000000	0,000000	-5,396708

Energy -9800.923567890 haretrees

1,4-diiodotetrafluorobenzene

		Coordinates (Angstroms)		
ATOM		X	Y	Z
1	C	1,411176	0,000000	0,000000
2	C	-1,411176	0,000000	0,000000
3	C	0,694993	1,193785	0,000000
4	C	0,694993	-1,193785	0,000000
5	C	-0,694993	-1,193785	0,000000
6	C	-0,694993	1,193785	0,000000
7	F	1,331113	2,369854	0,000000
8	F	-1,331113	2,369854	0,000000
9	F	-1,331113	-2,369854	0,000000
10	F	1,331113	-2,369854	0,000000
11	I	3,513417	0,000000	0,000000
12	I	-3,513417	0,000000	0,000000

Computed Frequencies (cm^{-1})

73.616, 123.313, 128.627, 129.985, 153.31, 157.911, 210.774, 236.401, 305.817, 314.354, 343.78, 395.888, 421.732, 445.34, 501.769, 593.127, 678.386, 691.532, 727.656, 745.81, 858.846, 968.615, 1142.069, 1219.889, 1302.766, 1396.916, 1441.343, 1486.263, 1613.672, 1624.057

Energy: -14467.179827416 hartrees

1,4-dibromotetrafluorobenzene

		Coordinates (Angstroms)		
ATOM		X	Y	Z
1	C	0,000000	0,000000	-1,406956
2	C	0,000000	0,000000	1,406956
3	C	-1,196714	0,000000	-0,695001
4	C	1,196714	0,000000	-0,695001
5	C	1,196714	0,000000	0,695001
6	C	-1,196714	0,000000	0,695001
7	F	-2,368097	0,000000	-1,334960
8	F	-2,368097	0,000000	1,334960
9	F	2,368097	0,000000	1,334960
10	F	2,368097	0,000000	-1,334960
11	Br	0,000000	0,000000	-3,295399
12	Br	0,000000	0,000000	3,295399

Computed frequencies (cm^{-1})

65.148, 125.022, 131.705, 138.455, 171.069, 196.263, 214.192, 273.151, 308.505, 311.28, 331.892, 387.938, 443.742, 457.683, 509.404, 599.196, 676.01, 682.387, 732.258, 793.889, 927.293, 974.471, 1148.763, 1244.929, 1300.843, 1417.706, 1460.316, 1499.238, 1623.558, 1633.266,

Energy: -5776.427097225 hartrees

1,4-diiodobenzene

	Coordinates (Angstroms)		
ATOM	X	Y	Z
1 C	1,386926	0,000000	0,000000
2 C	-1,386926	0,000000	0,000000
3 C	0,697365	1,210564	0,000000
4 C	0,697365	-1,210564	0,000000
5 C	-0,697365	-1,210564	0,000000
6 C	-0,697365	1,210564	0,000000
7 H	1,230614	2,153007	0,000000
8 H	1,230614	-2,153007	0,000000
9 H	-1,230614	-2,153007	0,000000
10 H	-1,230614	2,153007	0,000000
11 I	3,518748	0,000000	0,000000
12 I	-3,518749	0,000000	0,000000

Computed frequencies (cm^{-1})

95.545, 148.777, 157.459, 257.349, 295.908, 338.136, 407.229, 482.992, 636.917, 680.023, 694.568, 814.767, 830.914, 956.459, 978.811, 995.052, 1045.765, 1081.665, 1130.37, 1213.39, 1296.037, 1328.296, 1406.556, 1495.075, 1588.738, 1594.787, 3188.642, 3189.724, 3202.34, 3204.011

Energy: -14070.138432953 hartrees

1,4-dibromobenzene

	Coordinates (Angstroms)		
ATOM	X	Y	Z
1 C	0,000000	0,000000	-1,381391
2 C	0,000000	0,000000	1,381391
3 C	-1,211710	0,000000	-0,696950
4 C	1,211710	0,000000	-0,696950
5 C	1,211710	0,000000	0,696950
6 C	-1,211710	0,000000	0,696950
7 H	-2,149085	0,000000	-1,238242
8 H	2,149085	0,000000	-1,238242
9 H	2,149085	0,000000	1,238242
10 H	-2,149085	0,000000	1,238242
11 Br	0,000000	0,000000	-3,295821
12 Br	0,000000	0,000000	3,295821

Computed frequencies (cm^{-1})

81.242, 169.413, 215.377, 266.169, 315.535, 414.782, 433.841, 483.384, 637.915, 690.768, 729.927, 823.316, 826.606, 953.212, 976.38, 1019.636, 1082.058, 1094.661, 1127.759, 1202.988, 1302.724, 1321.018, 1411.604, 1501.045, 1601.936, 1605.693, 3197.508, 3198.542, 3210.706, 3212.417

Energy: -5379.391819103 hartrees

[1]: Spartan '08 V 1.2.0 © 1991-2009 Wavefunction Inc.

[2] Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* **8**, 3172 (2006).

2: Tables relative to solvent assisted grinding experiments

Table S2.1: FT-IR significant bands

	ORIGINAL	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
IEIB	2169,08	2159,97	2155,47	2168,27	2169,25	2169,15 [b]	2169,59 [b]	2167,35	2168,29	2162,61	2162,19	2156,96	2158,63	2153,18	2156,40	2157,29	2163,00	2169,10	2171,04 [b]	2161,31	2169,64	2163,81
	1477,02	1475,26	1476,49	1477,16	1477,18	1476,48	1476,96	1476,88	1477,40	1477,20	1479,33	1479,61	1486,71	1481,05	1479,88	1478,76	1476,78	1478,28	1478,02	1479,27	1478,03	1478,83
	1464,44	1459,90	1461,75	1463,98	1464,70	1458,78	1446,35	ND	1464,97	1456,85	1461,67	1468,23	1468,34	1467,61	1466,67	1461,15	1456,92	1465,38 [d]	1460,99	1458,06	1464,66	1470,60
	1386,83	1386,80	1386,24	1386,52	1385,96	1385,67	1385,50	1385,35	1387,74	1386,46	1387,81	1388,03	1388,36	1388,25	1388,12	1386,39	1385,56	1386,45	1386,36	1386,64	1383,04 [c]	1384,63
	1176,11	1181,24	1177,00	1176,07	1176,10	1179,75	1176,29	1176,17	1176,22	1179,50	1179,48	1174,44	1178,20	1179,96	1176,91	1168,96 [c]	1178,50	1175,69	1179,03	1169,55 [c]	1176,38	1179,03
	1056,52	1055,08	1055,08	1056,49	1056,18	1055,54	1036,59	1056,47	1056,71	1056,31	1056,68	1057,59	1059,41	1058,16	1057,14	1056,64	1053,27	1056,84	1055,22	1055,26	1056,82	1056,86
	1003,25	1001,22	1002,40	1003,78	1003,25	1002,20	1005,90	1005,95	1003,59	1000,62	1005,08	1003,99	1008,20	1006,27	1007,03	1004,06	1002,64	1005,91	1004,55	1006,09	1004,16	1005,26
	815,89	810,49	821,24	816,31	812,96	812,50	808,71	808,83	816,73	811,74	817,36	818,89	822,22	819,35	817,59	817,49	814,98	815,34	816,07	815,29	817,29	815,73
DIB	1461,74	1461,73	1461,65	1461,59	1462,75	1461,80	1462,01	1461,72	1461,75	1461,84	1461,82	1461,91	1464,76	1467,16	1466,57	1462,20	1461,69	1463,22	1461,75	1461,90	1461,91	1462,22
	1371,3	1371,12	1371,22	1371,49	1371,34	1371,13	1371,31	1371,21	1371,25	1371,59	1371,38	1373,22	1373,01	1374,85	1374,78	1371,08	1371,30	1371,44	1371,27	1371,55	1371,14	1372,09
	1067,69	1067,67	1068,20	1067,72	1067,64	1067,68	1068,12	1067,56	1067,84	1068,17	1067,75	1071,29	1059,82	1069,11	1067,60	1067,78	1067,72	1066,85	1067,83	1067,96	1067,98	1068,13
	991,92	991,92	991,99	991,75	992,12	992,44	993,01	992,55	991,83	992,68	992,58	993,67	989,39	994,80	994,80	992,77	991,88	996,23	992,63	993,10	993,33	992,87
	798,35	798,46	798,48	798,35	799,02	798,67	799,22	798,56	797,74	798,81	798,85	796,52	792,84	ND	ND	799,07	798,50	796,02	798,82	799,26	799,93	799,31
DITFB	1471,45	1475,51	1473,43	1460,38 [a]	1472,62	1472,04	1462,57 [a]	1473,09	1472,81	1462,59	1457,74 [a]	1458,42 [a]	1456,38 [a]	1454,3 [a]	1453,35 [a]	1463,25 [a]	1455,74 [a]	1460,34 [a]	1461,84 [a]	1457,5 [a]	1472,82	1462,29 [a]
	1459,33	1457,20	1457,75	1460,38 [a]	1459,60	1459,51	1462,57 [a]	1459,18	1459,21	1455,31	1457,74 [a]	1458,42 [a]	1456,38 [a]	1454,3 [a]	1453,35 [a]	1463,25 [a]	1455,74 [a]	1460,34 [a]	1461,84 [a]	1457,5 [a]	1459,89	1462,29 [a]
	1214,83	1206,67	1214,65	1213,68	1214,90	1214,91	1214,21	1214,18	1214,79	1214,94	ND	ND	1209,58	1205,17	1204,91	1210,73	1209,20	1214,12	1212,61	1212,81	1214,75	1213,37
	946,5	939,25 [a]	941,04 [a]	941,04 [a]	946,40	946,38	942,22 [a]	946,55	946,64	944,93	943,21 [a]	941,68 [a]	937,54 [a]	938,95 [a]	937,14 [a]	943,84 [a]	938,65 [a]	941 [a]	943,16 [a]	941,65 [a]	949,95 [c]	942,47 [a]
	941,28	939,25 [a]	941,04 [a]	941,04 [a]	941,36	941,57	942,22 [a]	941,32	941,12	938,90	943,21 [a]	941,68 [a]	937,54 [a]	938,95 [a]	937,14 [a]	943,84 [a]	938,65 [a]	942 [a]	943,16 [a]	941,65 [a]	941,18	942,47 [a]
	759,57	759,14	760,68	760,68	759,64	753,66	759,19	759,62	759,62	759,21	758,10	757,19	757,53	749,77	750,57	759,45	756,56	757,36	758,69	757,53	759,84	759,45
BEIB	2196,25	2196,66	2195,30	2195,14	2196,18	2196,55	2195,85	2197,18	2195,98	2196,14	2195,18	2197,84	2189,24	2188,24	2189,87	2194,75	2195,63	2193,69	2192,12	2195,94	2197,04	2196,05
	1478,37	1478,70	1478,59	1478,58	1478,47	1478,61	1478,63	1478,64	1478,49	1478,44	1478,54	1478,81	1479,82	1480,34	1480,93	1476,72	1478,53	1478,93	1478,65	1479,51	1478,47	1478,49
	1454,97	1454,69	1455,21	1454,73	1455,10	1455,30	1455,62	1455,80	1455,11	1456,24	1455,17	1455,17	1465,31	1463,82	1465,49	ND	1456,04	ND	1453,78	1456,42	1454,08	1447,51
	1386,45	1386,79	1386,53	1386,23	1386,45	1386,64	1386,63	1385,49	1386,51	1386,36	1386,59	1386,62	1388,64	1388,53	1388,78	1386,71	1386,28	1386,53	1386,73	1381,65	1385,89	1386,11
	1233,31	1232,96	1232,70	1233,53	1233,70	1233,77	1233,52	1234,08	1233,69	1233,89	1211,64 [d]	1233,07	1238,40	1236,30	1238,25	1235,51	1234,07	1234,35	1233,11	1234,01	1233,85	1234,71
	1054,7	1055,09	1054,81	1054,75	1054,85	1054,99	1054,91	1054,85	1054,75	1054,71	1054,57	1054,91	1060,54	1058,36	1058,38	1055,24	1054,79	1057,82	1054,82	1055,14	1054,81	1055,78
	1005,59	1006,06	1005,53	1005,71	1006,03	1005,53	1005,95	1006,04	1005,86	1006,18	1005,93	1006,90	1009,10	1006,84	1008,21	1006,42	1004,88	1008,37	1006,14	1006,38	1005,98	1006,31
	810,76	812,17	811,56	811,68	811,31	812,22	811,97	812,13	811,95	811,43	811,82	812,75	810,29	815,72	817,06	812,69	812,57	814,36	812,27	813,63	811,90	812,74
DBB	1465,88	1465,87	1465,71	1465,82	1465,73	1465,72	1465,87	1465,84	1465,75	1465,05	1465,74	1466,28	1465,85	1465,80	1465,84	1465,44	1465,75	1465,78	1465,72	1465,48	1465,97	1466,17
	1381,23	1381,47	1381,37	1381,23	1381,34	1381,36	1381,41	1384,48	1381,15	1381,20	1381,42	1380,08	1381,54	1381,18	1381,23	1380,86	1381,28	1381,33	1381,42	ND	ND	1380,40
	1065,311	1065,24	1065,11	1065,24	1065,10	1065,17	1065,38	1065,28	1065,23	1065,50	1065,12	1066,33	1065,27	1065,39	1065,32	1065,32	1065,13	1065,20	1065,33	1064,88	1065,41	1066,77
	1003,16	1003,03	1002,90	1003,11	1003,01	1003,50	1002,21	1003,10	1003,10	1003,37	1003,01	1003,47	1003,04	1003,19	1003,02	1003,70	1003,00	1003,11	1003,14	1003,42	1003,23	1003,25
	807,42	806,73	806,69	807,13	806,72	806,82	806,85	807,04	806,82	807,15	806,85	807,58	804,29	807,67	807,05	807,06	806,75	806,89	807,03	807,28	807,36	806,48
DBTFB	1494,44	1479,08 [a]	1481,72 [a]	1492,82 [d]	1493,19	1492,79	1493,47	1493,05 [d]	1492,90	1486,53 [a]	1490,65 [a]	1485,06 [a]	1478,23 [a]	1475,55 [a]	1476,39 [a]	1476,17 [a]	1493,37	1480,95 [a]	1479,91 [a]	1487,65 [a]	1483,99 [d]	1479,5 [a]
	1480,72	1479,08 [a]	1481,72 [a]	1479,47 [d]	1480,15	1480,00	1483,44	1488,59 [d]	1482,00	1486,53 [a]	1490,65 [a]	1485,06 [a]	1478,23 [a]	1475,55 [a]	1476,39 [a]	1476,17 [a]	1480,18	1480,95 [a]	1479,91 [a]	1487,65 [a]	1484,99 [d]	1479,5 [a]
	1448,76	1448,89	1452,23	1448,80	1448,71	1448,71	1447,98	1448,59	1448,63	1450,79	1448,95	1449,20	1447,28	1450,53	ND	1448,95	1448,76	1448,35	1448,58	1442,23	1448,66	1448,68
	1234,87	1230,38	1231,90	1234,81	1234,65	1234,89	1235,21	1235,02	1234,70	ND	ND	1232,20	1230,48	1232,54	1229,34	1239,08 [c]	1234,84	1235,91	1231,05	ND	1234,88	1234,98
	989,4	991,78	987,97	989,48	989,56	989,16	ND	ND	987,84	988,38	989,65	985,86	989,21	994,09	995,34	988,86	989,50	986,73 [c]	990,76	ND	993,4 [c]	990,34
	954,17	952,79	952,71	954,16	954,53	954,02	954,54	953,70	954,20	956,57	954,76	952,96	952,65	953,53	952,52	955,43	954,41	953,76	954,47	ND	957,16 [c]	955,37
	788,05	787,32	790,51	787,89	787,80	788,04	788,33	786,02	789,65	790,77	788,42	787,75	785,28	785,33	784,76	788,64	788,05	788,58	787,59	ND	788,71	789,10
	774,72	774,21	774,10	775,50	775,24	775,48	775,05	770,97	ND	771,05	774,30	778,48	771,81	770,01	769,80	775,34	775,24	775,49	774,71	774,02	774,65	ND

frequencies are expressed in wavenumbers (cm^{-1})

[a]: the two bands in the spectrum of the pure compound appear as a single band in the spectrum of the product. The frequency of this band is reported.

[b]: the band is very weak and its position cannot be assigned precisely.

[c]: the band is covered by a band of the acceptor, therefore its position is unreliable.

[d]: broaden

ND: the band cannot be detected in the spectrum.

Table S2.2: table of band shifts

	ORIGINAL	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
IEIB	2169,08	-9,1	-13,6	-0,8	0,2	0,1 [b]	0,5 [b]	-1,7	-0,8	-6,5	-6,9	-12,1	-10,4	-15,9	-12,7	-11,8	-6,1	0,0	2,0 (b)	-7,8	0,6	-5,3
	1477,02	-1,8	-0,5	0,1	0,2	-0,5	-0,1	-0,1	0,4	0,2	2,3	2,6	9,7	4,0	2,9	1,7	-0,2	1,3	1,0	2,3	1,0	1,8
	1464,44	-4,5	-2,7	-0,5	0,3	-5,7	-18,1	ND	0,5	-7,6	-2,8	3,8	3,9	3,2	2,2	-3,3	-7,5	0,9 [d]	-3,5	-6,4	0,2	6,2
	1386,83	0,0	-0,6	-0,3	-0,9	-1,2	-1,3	-1,5	0,9	-0,4	1,0	1,2	1,5	1,4	1,3	-0,4	-1,3	-0,4	-0,5	-0,2	-3,8 [c]	-2,2
	1176,11	5,1	0,9	0,0	0,0	3,6	0,2	0,1	0,1	3,4	3,4	-1,7	2,1	3,9	0,8	-7,1 [c]	2,4	-0,4	2,9	-6,6 [c]	0,3	2,9
	1056,52	-1,4	-1,4	0,0	-0,3	-1,0	-19,9	0,0	0,2	-0,2	0,2	1,1	2,9	1,6	0,6	0,1	-3,3	0,3	-1,3	-1,3	0,3	0,3
	1003,25	-2,0	-0,9	0,5	0,0	-1,0	2,6	2,7	0,3	-2,6	1,8	0,7	5,0	3,0	3,8	0,8	-0,6	2,7	1,3	2,8	0,9	2,0
	815,89	-5,4	5,4	0,4	-2,9	-3,4	-7,2	-7,1	0,8	-4,1	1,5	3,0	6,3	3,5	1,7	1,6	-0,9	-0,5	0,2	-0,6	1,4	-0,2
DIB	1461,74	0,0	-0,1	-0,2	1,0	0,1	0,3	0,0	0,0	0,1	0,1	0,2	3,0	5,4	4,8	0,5	0,0	1,5	0,0	0,2	0,2	0,5
	1371,3	-0,2	-0,1	0,2	0,0	-0,2	0,0	-0,1	0,0	0,3	0,1	1,9	1,7	3,5	3,5	-0,2	0,0	0,1	0,0	0,3	-0,2	0,8
	1067,69	0,0	0,5	0,0	0,0	0,0	0,4	-0,1	0,1	0,5	0,1	3,6	-7,9	1,4	-0,1	0,1	0,0	-0,8	0,1	0,3	0,3	0,4
	991,92	0,0	0,1	-0,2	0,2	0,5	1,1	0,6	-0,1	0,8	0,7	1,8	-2,5	2,9	2,9	0,9	0,0	4,3	0,7	1,2	1,4	1,0
	798,35	0,1	0,1	0,0	0,7	0,3	0,9	0,2	-0,6	0,5	0,5	-1,8	-5,5	ND	ND	0,7	0,1	-2,3	0,5	0,9	1,6	1,0
DITFB	1471,45	4,1	2,0	-11,0 [a]	1,2	0,6	-8,8 [a]	1,6	1,4	-8,9	-13,7 [a]	-13,0 [a]	-15,1 [a]	-17,2 [a]	-18,1 [a]	-8,2	-15,7 [a]	-11,1 [a]	-9,6 [a]	-14,0 [a]	1,4	-9,2 [a]
	1459,33	-2,1	-1,6	1,1 [a]	0,3	0,2	3,2 [a]	-0,2	-0,1	-4	-1,6 [a]	-0,9 [a]	-3,0 [a]	-5,0 [a]	-6,0 [a]	3,9 [a]	-3,6 [a]	1,0 [a]	2,5 [a]	-1,8 [a]	0,6	3,0 [a]
	1214,83	-8,2	-0,2	-1,1	0,1	0,1	-0,6	-0,6	0,0	0,1	-3,3	-4,8	-5,3	-9,7	-9,9	-4,1	-5,6	-0,71	-2,2	-2	-0,1	-1,5
	946,5	-7,3 [a]	-5,5 [a]	-5,5 [a]	-0,1	-0,1	-4,3 [a]	0,1	0,1	-1,6	-3,3 [a]	-4,8 [a]	-9,0 [a]	-7,6 [a]	-9,4 [a]	-2,7 [a]	-7,9 [a]	-4,5 [a]	-3,3 [a]	-4,9 [a]	3,5 [c]	-4,0 [a]
	941,28	-2, [a]	-0,2 [a]	-0,2 [a]	0,1	0,3	0,9 [a]	0	0,2	-2,4	1,9 [a]	0,4 [a]	-3,7 [a]	-2,3 [a]	-4,1 [a]	2,6 [a]	-2,6 [a]	0,7 [a]	1,9 [a]	0,4 [a]	-0,1	1,2 [a]
	759,57	-0,4	1,1	1,1	0,1	-5,9	-0,4	0,0	0,0	-0,4	-1,5	-2,4	-2,0	-9,8	-9,0	-0,1	-3,0	-2,2	-0,9	-2,0	0,3	-0,1
BEIB	2196,25	0,4	-0,9	-1,1	-0,1	0,3	-0,4	0,9	-0,3	-0,1	-1,1	1,6	-7,0	-8,0	-6,4	-1,5	-0,6	-2,6	-4,1	-0,3	0,8	-0,2
	1478,37	0,3	0,2	0,2	0,1	0,2	0,3	0,3	0,1	0,1	0,2	0,4	1,5	2,0	2,6	-1,6	0,2	0,6	0,3	1,1	0,1	0,1
	1454,97	-0,3	0,2	-0,2	0,1	0,3	0,6	0,8	0,1	1,3	0,2	0,2	10,3	8,8	10,5	ND	1,1	ND	-1,2	1,5	-0,9	-7,5
	1386,45	0,3	0,1	-0,2	0,0	0,2	0,2	-1,0	0,1	-0,1	0,1	0,2	2,2	2,1	2,3	0,3	-0,2	0,1	0,3	-4,8	-0,6	-0,3
	1233,31	-0,3	-0,6	0,2	0,4	0,5	0,2	0,8	0,4	0,6	-21,7	-0,2	5,1	3,0	4,9	2,2	0,8	1,0	-0,2	0,7	0,5	1,4
	1054,7	0,4	0,1	0,0	0,1	0,3	0,2	0,1	0,0	0,0	-0,1	0,2	5,8	3,7	3,7	0,5	0,1	3,1	0,1	0,4	0,1	1,1
	1005,59	0,5	-0,1	0,1	0,4	-0,1	0,4	0,4	0,3	0,6	0,3	1,3	3,5	1,3	2,6	0,8	-0,7	2,8	0,5	0,8	0,4	0,7
	810,76	1,4	0,8	0,9	0,5	1,5	1,2	1,4	1,2	0,7	1,1	2,0	-0,5	5,0	6,3	1,9	1,8	3,6	1,5	2,9	1,1	2,0
DBB	1465,88	0,0	-0,2	-0,1	-0,2	-0,2	0,0	0,0	-0,1	-0,8	-0,1	0,4	0,0	-0,1	0,0	-0,4	-0,1	-0,1	-0,2	-0,4	0,1	0,3
	1381,23	0,2	0,1	0,0	0,1	0,1	0,2	3,3	-0,1	0,0	0,2	-1,2	0,3	0,0	0,0	-0,4	0,0	0,1	0,2	ND	ND	-0,8
	1065,311	-0,1	-0,2	-0,1	-0,2	-0,1	0,1	0,0	-0,1	0,2	-0,2	1,0	0,0	0,1	0,0	0,0	-0,2	-0,1	0,0	-0,4	0,1	1,5
	1003,16	-0,1	-0,3	0,0	-0,1	0,3	-0,9	-0,1	-0,1	0,2	-0,1	0,3	-0,1	0,0	-0,1	0,5	-0,2	0,0	0,0	0,3	0,1	0,1
	807,42	-0,7	-0,7	-0,3	-0,7	-0,6	-0,6	-0,4	-0,6	-0,3	-0,6	0,2	-3,1	0,3	-0,4	-0,4	-0,7	-0,5	-0,4	-0,1	-0,1	-0,9
DBTFB	1494,44	-15,4 [a]	-12,7 [a]	-1,6 [d]	-1,3	-1,7	-1,0	-1,4 [d]	-1,5	-7,9 [a]	-3,8	-9,4 [a]	-16,2 [a]	-18,9 [a]	-18,1 [a]	-18,3 [a]	-1,1	-13,5 [a]	-14,5 [a]	-6,8 [a]	-1,5 [d]	-14,9 [a]
	1480,72	-1,6 [a]	1,0[a]	-1,3 [d]	-0,6	-0,7	2,7	7,9 [d]	1,3	5,8 [a]	9,9	4,3 [a]	-2,5 [a]	-5,2 [a]	-4,3 [a]	-4,6 [a]	-0,5	0,2 [a]	-0,8 [a]	6,9 [a]	4,3 [d]	-1,2 [a]
	1448,76	0,1	3,5	0,0	0,0	0,0	-0,8	-0,2	-0,1	2,0	0,2	0,4	-1,5	1,8	ND	0,2	0,0	-0,4	-0,2	-6,5	-0,1	-0,1
	1234,87	-4,5	-3,0	-0,1	-0,2	0,0	0,3	0,2	-0,2	ND	ND	-2,7	-4,4	-2,3	-5,5	4,2 [c]	0,0	1,0	-3,8	ND	0,0	0,1
	989,4	2,4	-1,4	0,1	0,2	-0,2	ND	ND	-1,6	-1,0	0,3	-3,5	-0,2	4,7	5,9	-0,5	0,1	-2,7 [c]	1,4	ND	4,0 [c]	0,9
	954,17	-1,4	-1,5	0,0	0,4	-0,1	0,4	-0,5	0,0	2,4	0,6	-1,2	-1,5	-0,6	-1,6	1,3	0,2	-0,4	0,3	ND	3,0 [c]	1,2
	788,05	-0,7	2,5	-0,2	-0,3	0,0	0,3	-2,0	1,6	2,7	0,4	-0,3	-2,8	-2,7	-3,3	0,6	0,0	0,5	-0,5	ND	0,7	1,1
	774,72	-0,5	-0,6	0,8	0,5	0,8	0,3	-3,8	ND	-3,7	-0,4	3,8	-2,9	-4,7	-4,9	0,6	0,5	0,8	0,0	-0,7	-0,1	ND

band shifts are expressed in Δ cm^{-1} ($Wn_{cocrystal} - Wn_{donor}$)

green: evidence of co-crystal formation; red: no evidence of co-crystal formation

[a]: the two bands in the spectrum of the pure compound appear as a single band in the spectrum of the product. The frequency of this band is reported

[b]: the band is very weak and its position cannot be assigned precisely.

[c]: the band is covered by a band of the acceptor, therefore its position is unreliable.

[d]: broaden

ND: the band cannot be detected in the spectrum

Experimental details:

Spectra were acquired using a Thermo Nicolet Nexus 380 FT-IR spectrometer equipped with the Smart Performer ATR device. A standard Ge ATR crystal was used for acquiring spectra of co-crystallization products containing DITFB, DBTFB, DIB and DBB, while in order to enhance the instrument sensitivity in the 2000-2300 cm^{-1} region where the triple bond stretching band can be found a ZnSe ATR crystal was used to perform the analysis of products containing IEIB and BEIB. Bands position was assigned automatically using Omnic 7.3.[2]

Spectral analysis:

Spectra of products were compared with those of the corresponding pure donor and acceptor. For each donor the bands which appeared to be the most sensitive to the cocrystal formation were selected and their shift collected and analyzed (Table S2.2). The occurrence of a positive co-crystallization event was determined if at least two bands in the product that are related to the XB donor were shifted of more than 1 cm^{-1}. Further spectra visual inspections were conducted in order to precisely identify the presence of peaks shifts in ambiguous cases (in particular those indicated with [b], [c] and [d] notes).

Comments:

The most evident effect of the halogen bonding occurrence in compounds IEIB and BEIB is the shift in the band corresponding to the triple bond stretching (2169 and 2196 cm^{-1} respectively), even if in some case this band appears weak and broad, not allowing the perfect determination of its position. Before confirming the formation of a cocrystal however other proofs, i.e. the presence of further bandshifts, were also necessary.

In the case of fluorinated compounds the major evidence of the occurrence of an interaction is the behaviour of the bands at 1471,4and 1459,33 in the case of DITFB and 1494,44 and 1480,72 in the case of DBTFB, that collapse in a single band usually red-shifted with respect to the lowest frequency band. It's possible to observe the same behaviour also for the bands at 946,5 and 941,28 for DITFB and at 989,4 and 954,17 for DBTFB. Before confirming the formation of a cocrystal however other proofs, i.e. the presence of further bandshifts, were also necessary.

In DIB none of the bands is strongly influenced by the presence of an interaction with the acceptors, but usually it was possible to observe small changes in several peaks, especially around 1000 cm^{-1}.

In the DBB case, spectra show a perfect match with the sum of the starting materials ones.

[2] Omnic 7.3 © 1992-2006 Thermo Electron Corporation.

3: Single crystal data

Experimental

Datasets were collected on a Bruker SMART APEX II system with Mo radiation at 120 K using APEX2 software.[3] An Oxford Croystream 700 low-temperature device was used to control temperature. MoKα radiation was used. Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[4] Scan speeds and scan widths were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrices were improved by least-squares refinement of reflections thresholded from the entire dataset. Integrations were performed with SAINT,[5] using these improved unit cells as a starting point. Precise unit cell constants were calculated in SAINT from the final merged datasets. Lorenz and polarization corrections were applied. Absorption corrections was applied using SADABS[6] Friedel opposites for the noncentrosymmetric structure **7** were not merged.

Datasets were reduced with SHELXTL.[7] The structures were solved by direct methods without incident. All hydrogen atoms were assigned to idealized positions and were allowed to ride. Isotropic thermal parameters for the hydrogen atoms were constrained to be 1.5x (methyl) / 1.2x (all other) that of the connected atom.

[3] APEXII v2009. 5-1, © 2009, Bruker Analytical X-ray Systems, Madison, WI.

[4] COSMO v1. 60, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.

[5] SAINT v7. 60a, © 1997 - 2008, Bruker Analytical X-ray Systems, Madison, WI.

[6] SADABS v2008/1, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

[7] SHELXTL v2008/4, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

Table S3 Crystallographic parameters

	IEIB:19	**IEIB:2**	**IEIB:11**	**7**
Systematic name	MKA_A20 [1-iodo-4-(iodoethynyl)benzene]$_2$, 1,4-bis[(1-benzimidazolyl)-methyl]-benzene	MKA_A2 1-iodo-4-(iodoethynyl)-benzene, 4-phenylpyridine	MKA_A19 1-iodo-4-(iodoethynyl)-benzene, 1-[(4-bromophenyl)-methyl]-5,6-dimethyl-benzimidazole	MKA_D2 1-iodo-4-(bromoethynyl)benzene
Formula moiety	$(C_8H_4I_2)_2$ $(C_{22}H_{18}N_4)$	$(C_8H_4I_2)$ $(C_{11}H_9N)$	$(C_8H_4I_2)$ $(C_{16}H_{15}BrN_2)$	C8 H4 Br I
Empirical formula	$C_{38}H_{26}I_4N_4$	$C_{19}H_{13}I_2N$	$C_{24}H_{19}BrI_2N_2$	C_8H_4BrI
Molecular weight	1046.23	509.10	669.12	306.92
Color, Habit	yellow rod	colourless plate	colourless rod	colourless plate
Crystal size/mm	0.32 x 0.12 x 0.06	0.30 x 0.22 x 0.04	0.36 x 0.10x 0.06	0.04 x 0.28 x 0.34
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group, Z	P2(1)/n, 2	P-1, 2	P2(1)/c, 4	$Pna2_1$, 4
a, Å	11.8228(6)	7.3548(4)	15.9781(7)	33.594(3)
a, Å	6.0776(3)	9.7489(5)	5.9393(3)	4.0898(3)
a, Å	24.7764(12)	13.2570(7)	24.1672(11)	5.9859(4)
α, °	90.00	107.2200(10)	90.00	90.00
β, °	91.2900(10)	102.782(2)	91.491(2)	90.00
γ, °	90.00	99.708(2)	90.00	90.00
Volume, Å^3	1779.84(15)	857.01(8)	2292.66(19)	822.42(10)
X-ray wavelength	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	3.534	3.665	4.499	8.669
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan
trans min / max	0.3976 / 0.8159	0.4060 / 0.8672	0.2942 / 0.7741	0.1566 / 0.7230
Reflections				
collected	21072	18011	24217	6711
independent	6160	5291	8007	2205
observed	5641	4687	5947	2024
Threshold expression	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)
R_1 (observed)	0.0201	0.0239	0.0365	0.0944
wR_2 (all)	0.0508	0.0616	0.0829	0.0923
S	0.986	1.084	0.996	1.928 / -1.100
Δρ max / min	0.824 / -0.467	0.814 / -0.876	0.974 / -0.865	0.052(16)

5. Color version of Figures:

Figure 2: From left to right and from top to bottom, the molecules object of this study in order of decreasing surface electrostatic potential associated to the σ-hole of the best XB donor atom in the molecule. In evidence the electrostatic potential surfaces, calculated at 0.002 IsoValue. Potential values are in kJ/mol.

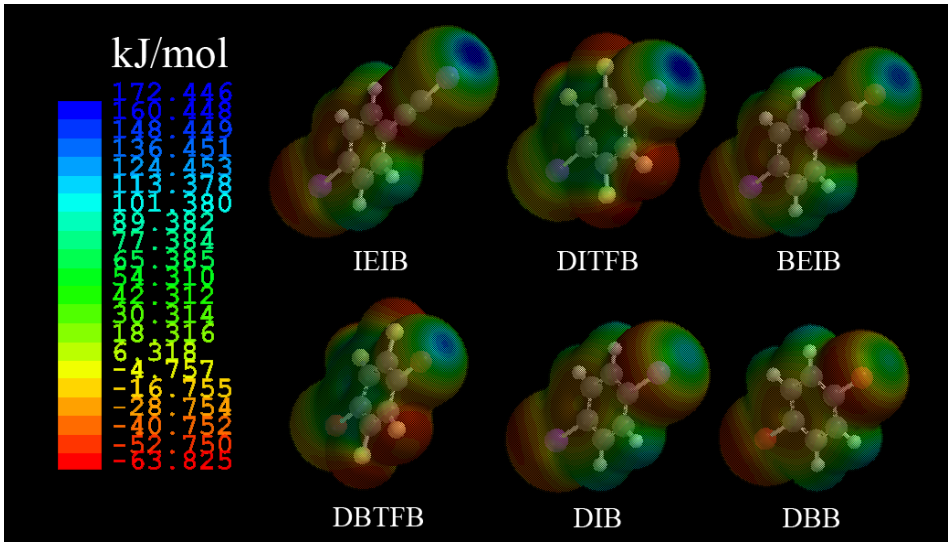

Figure 5: A sample comparison between the ATR-FTIR spectra of a XB donor as pure (**IEIB**, top blue line) and of the product of a successful co-grinding experiment (**IEIB:12** cocrystal, bottom red line). The position of relevant peaks of the XB donor and the new position of the same in the spectrum of the product are also reported.

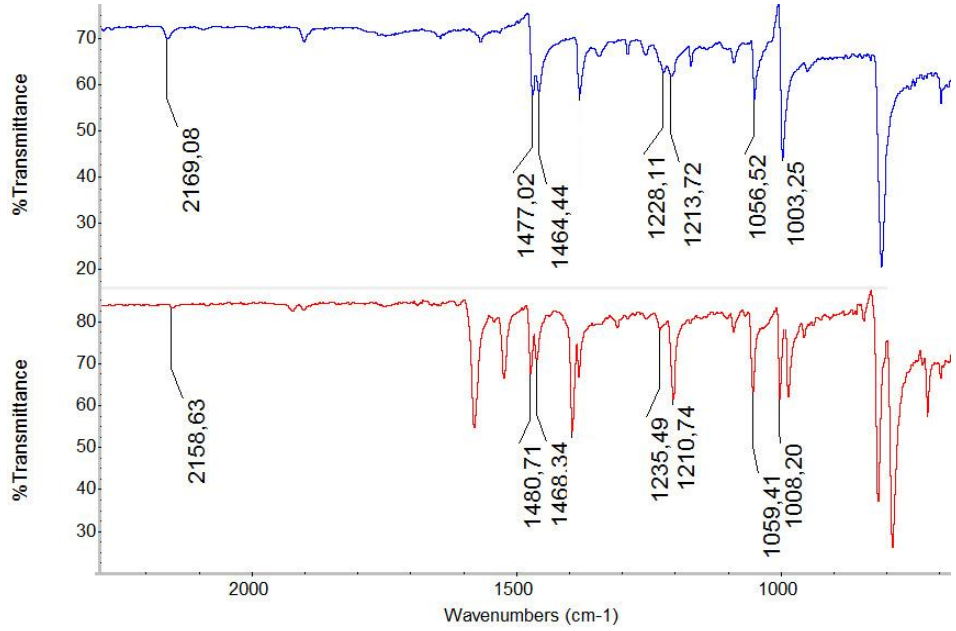

Figure 7. Crystal structure of the **IEIB:2** cocrystal. In evidence the primary intramolecular contacts (black dotted lines), represented by the I···N XB and the Type I contact between the two Csp^2-bound iodine atoms. The iodoethynyl moiety is interacting with the major electrondonor site (the pyridyl nitrogen), driving the formation of the cocrystal. Color code: carbon, gray; hydrogen, light gray; nitrogen, blue; iodine, violet.

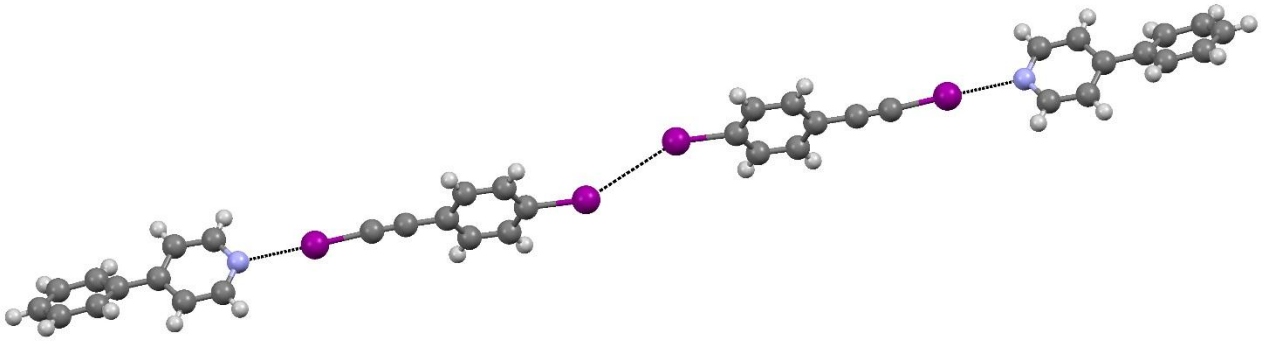

Figure 8. Intermolecular contacts (dotted black lines) in the **IEIB:11** cocrystal. In picture a), the supramolecular adduct formed by the interaction of the XB sonors donors of **IEIB** and the acceptors of compound **11**. In picture b) Type I halogen-halogen contacts among Br atoms of compound **11** and the halogen bond between the most activated iodine atom of **IEIB** and the nitrogen of compound **11**. Color code: carbon, grey; hydrogen, light gray; nitrogen, blue; bromine, orange; iodine, violet.

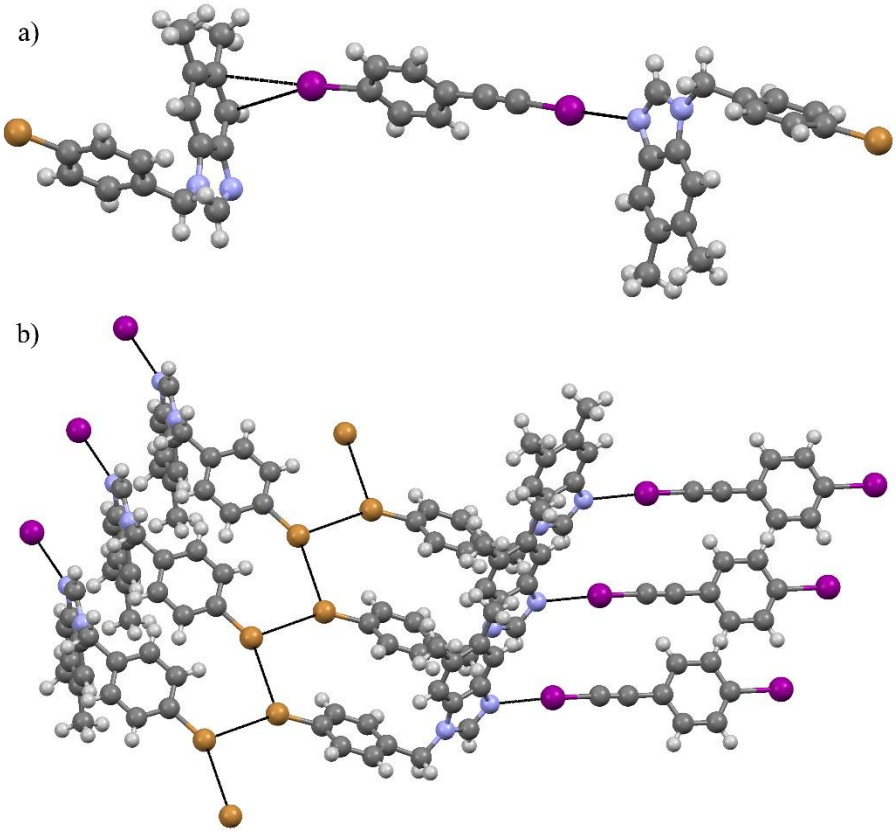

Figure 9. Crystal structure of the halogen bonded supramolecular adduct **IEIB:19**. In evidence in picture a) the primary I···N halogen bond and the secondary C-I···π halogen bond (black dotted lines). Color code as in Figure 3. In picture b) a spacefill representation of the interpenetration between the different nets. To each color corresponds a different net. In picture c) a simplified representation of the interpenetrating networks; the topological analysis and the picture were obtained using TOPOS 4.0.[18]

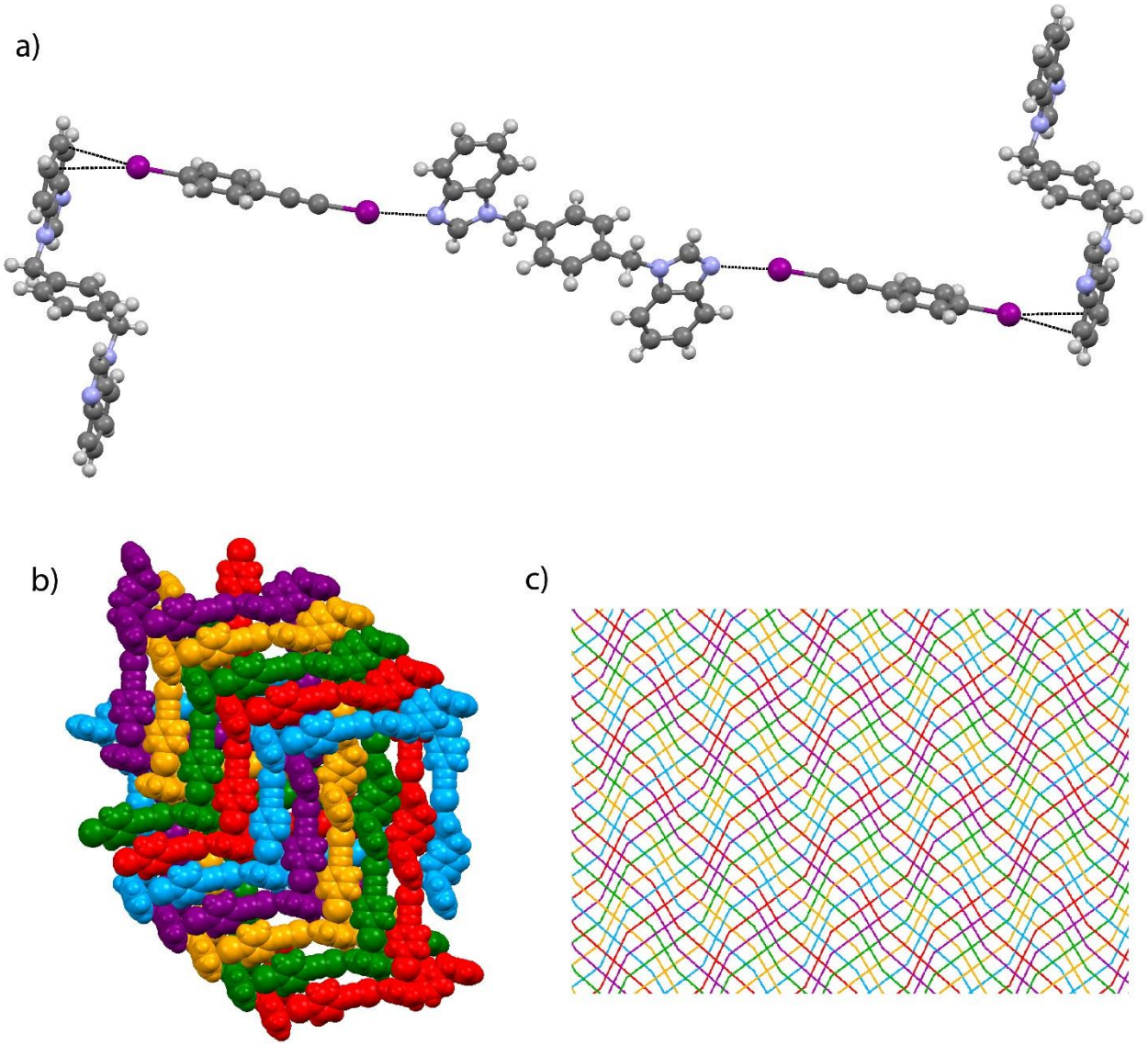

Figure 10. Crystal structure of pure **BEIB**. A linear halogen bond (black dotted lines) among Br atom and the π electron cloud of the alkyne, almost perpendicular to the C≡C bond axis, represent the major noncovalent interaction among **BEIB** molecules. Color code as in Figure 5.