crystals

MDPI

Supplementary Information

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II General Synthesis method

Table S1 Summary of crystallization experiments

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
DI2	×	×	×	×	B	A	B′	C
DI4	×	A′	A′′	B (**I**), D (**II**)	B′	×	B	×
DI6	A	×	×	×	B	×	B	A
DI8	A	×	A	×	×	×	A	×

×Unsuccessful crystallization

1. Method A

To a solution of acceptor (0.10 mmol) in chloroform (0.5 ml), was added donor (0.10 mmol) at room temperature. The solution was left at room temperature, and subjected to slow evaporation to give colourless crystals.

2. Method A′

To the oil substances obtained from **Method A,** was added 0.5 ml of methanol and left at room temperature to slow evaporation to give colourless crystals.

2. Method A′′

To the oil substances obtained from **Method A′,** was added 1:1 ratio (0.5 ml, v/v) of dichloromethane:diethylether, and left at room temperature to slow evaporation to give colourless crystals.

2. Method B

Solutions of acceptor (0.15 mmol) in chloroform (0.800 ml) and of DI6 (0.17 mmol) in chloroform (0.330 ml) were prepared. To a 0.25 ml aliquot of acceptor solution was added liquid DI2 (14.0 μl, 0.10 mmol), DI4 (18.6 μl, 0.10 mmol) or an aliquot (0.10 ml) of the DI6 solution. The resulting solution was left at room temperature, and subjected to slow evaporation to give colourless crystals.

3. Method B′

The crystals obtained by **Method B** were re-dissolved in 0.10 ml of acetonitrile. The resulting solution was left at room temperature, and subjected to slow evaporation to give colourless crystals.

4**. Method C**

The sample vial containing oil substances obtained from **Method A′′** was placed over liquid nitrogen taken in dewar flask to give immediate colourless plate crystals.

5. Method D

To the solid acceptor (0.05 – 0.10 mmol) was added liquid **DI2** (27.2 μl, 0.20 mmol) or **DI4** (18.4 μl, 0.10 mmol). The resulting suspension was briefly (1-2 minutes) sonicated. The colourless crystals were obtained immediately or after a few days.

Table S2. Crystal data and X-Ray experimental details for **1•DI6** - **3•DI8**

Complex	**1•DI6**	**1•DI8**	**2•DI4**	**3•DI4**	**3•DI8**
CCDC Number	1554409	1554410	1554411	1554412	1554413
Empirical formula	$C_{11}H_5F_{12}I_2NO$	$C_{13}H_5F_{16}I_2NO$	$C_{10}H_7F_8I_2NO$	$C_{10}H_7F_8I_2NO$	$C_{14}H_7F_{16}I_2NO$
Formula weight	648.96	748.98	562.97	562.97	763.01
Temperature (K)	170.0(1)	170.0(1)	170.0(1)	170.0(1)	120.0(1)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*Pbcn*	$P\bar{1}$	$P2_1/c$
Unit cell dimensions: *a* (Å)	27.477(6)	31.467(6)	5.6354(11)	8.0850(16)	7.3797(4)
b (Å)	8.8138(18)	8.8729(18)	13.829(3)	8.8911(18)	9.7730(5)
c (Å)	7.2973(15)	7.3245(15)	20.202(4)	11.921(2)	29.5688(17)
α (°)	90	90	90	73.40(3)	90
β (°)	102.85(3)	100.08(3)	90	83.90(3)	95.812(5)
γ (°)	90	90	90	73.32(3)	90
Volume (Å^3)	1722.9(6)	2013.4(7)	1574.4(5)	786.4(3)	2121.6(2)
Z	4	4	4	2	4
Density (calculated) (mg m^{-3})	2.502	2.471	2.375	2.377	2.389
Absorption coefficient (mm^{-1})	3.775	3.276	4.076	4.080	3.111
F(000)	1200	1392	1040	520	1424
Crystal size (mm^3)	0.13×0.12×0.09	0.43×0.22×0.20	0.17×0.14×0.10	0.23×0.17×0.14	0.23×0.15×0.14
θ range for data collection (°)	2.43 to 25.25	2.39 to 25.25	2.02 to 25.25	2.48 to 25.25	3.22 to 25.25
Reflections collected	19204	6664	10674	5917	13866
[*R*(int)]	[0.0295]	[0.0286]	[0.0304]	[0.0281]	[0.0477]
Reflections [$I > 2\sigma(I)$]	1519	1655	1244	2378	3500
Data completeness (%)	99.8	99.8	99.9	99.6	99.8
Data/restraints/ parameters	1561/0/124	1829/0/151	1426/0/121	2842/0/200	3831/90/371
Goodness-of-fit on F^2	1.177	1.071	1.047	1.053	1.267
Final *R* indices	R_1 = 0.0200,	R_1 = 0.0235,	R_1 = 0.0181,	R_1 = 0.0311,	R_1 = 0.0823,
[$I > 2\sigma(I)$]	wR_2 = 0.0481	wR_2 = 0.049	wR_2 = 0.0382	wR_2 = 0.0644	wR_2 = 0.1749
Final *R* indices	R_1 = 0.0208,	R_1 = 0.0275,	R_1 = 0.0231,	R_1 = 0.0396,	R_1 = 0.0897,
[all data]	wR_2 = 0.0485	wR_2 = 0.0510	wR_2 = 0.0404	wR_2 = 0.0680	wR_2 = 0.1778
Largest diff. peak/hole (*e* Å^{-3})	0.466/−0.576	0.533/−0.383	0.387/−0.268	0.540/−0.692	2.064/−2.030

52 **Table S3.** Crystal data and X-Ray experimental details for **4•DI4_I - 5•DI6**

Complex	**4•DI4_I**	**4•DI4_II**	**5•DI2**	**5•DI4**	**5•DI6**
CCDC Number	1554414	1554415	1554416	1554417	1554418
Empirical formula	$C_{10}H_7F_8I_2NO$	$C_{10}H_7F_8I_2NO$	$C_9H_9F_4I_2NO$	$C_{18}H_{18}F_8I_2N_2O_2$	$C_{13}H_9F_{12}I_2NO$
Formula weight	562.97	562.97	476.97	700.14	677.01
Temperature (K)	170.0(1)	170.0(1)	253.0(1)	170.0(1)	123.0(1)
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	*Pbcn*	*P*2/*c*	$P\bar{1}$	$P2_1/n$
Unit cell dimensions: *a* (Å)	8.10920(10)	7.3783(2)	6.4650(5)	7.6208(2)	20.6798(6)
b (Å)	9.2775(2)	11.2330(3)	9.4509(6)	8.3262(2)	9.83442(17)
c (Å)	11.6989(2)	19.2195(3)	12.1746(7)	10.2556(2)	20.7164(5)
α (°)	73.3431(9)	90	90	76.4230(11)	90
β (°)	82.1250(10)	90	95.268(6)	80.7069(11)	112.193(3)
γ (°)	70.7346(10)	90	90	66.4880(10)	90
Volume (Å^3)	795.12(2)	1592.92(7)	740.73(9)	578.36(2)	3901.05(18)
Z	2	4	2	1	8
Density (calculated) (mg m^{-3})	2.351	2.347	2.139	2.010	2.305
Absorption coefficient (mm^{-1})	4.036	4.029	4.289	2.800	3.338
F(000)	520	1040	440	334	2528
Crystal size (mm^3)	0.686×0.292×0.230	0.254×0.251×0.238	0.351×0.226×0.080	0.584×0.239×0.201	0.667×0.214×0.145
θ range for data collection (°)	2.664 to 27.842	2.119 to 28.881	3.164 to 28.872	2.716 to 27.869	2.953 to 28.784
Reflections collected [*R*(int)]	12799 [0.0285]	30250 [0.0484]	2724 [0.0154]	10383 [0.0299]	51374 [0.0282]
Reflections [$I > 2\sigma(I)$]	3429	1484	1231	2550	8826
Data completeness (%)	96.7	100.0	99.3	99.9	99.8
Data/restraints/ parameters	3630/692/329	2081/293/158	1641/181/108	2708/658/259	9421/0/528
Goodness-of-fit on F^2	1.082	1.057	1.042	1.062	1.101
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0200, wR_2 = 0.0473	R_1 = 0.0331, wR_2 = 0.0583	R_1 = 0.0590, wR_2 = 0.1834	R_1 = 0.0194, wR_2 = 0.0424	R_1 = 0.0197, wR_2 = 0.0428
Final *R* indices [all data]	R_1 = 0.0217, wR_2 = 0.0481	R_1 = 0.0518, wR_2 = 0.0647	R_1 = 0.0739, wR_2 = 0.2014	R_1 = 0.0213, wR_2 = 0.0431	R_1 = 0.0235, wR_2 = 0.0454
Largest diff. peak/hole (*e* Å^{-3})	0.475/−0.431	0.392/−0.439	1.471/−1.124	0.364/−0.333	0.780/−0.653

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54 **Table S4.** Crystal data and X-Ray experimental details for **6•DI2 - 7•DI8**

Complex	**6•DI2**	**7•DI2**	**7•DI4**	**7•DI6**	**7•DI8**
CCDC Number	1554419	1554420	1554421	1554422	1554423
Empirical formula	$C_{16}H_{18}F_4I_2N_2O_2$	$C_{16}H_{18}F_4I_2N_2O_2$	$C_{11}H_9F_8I_2NO$	$C_{13}H_9F_{12}I_2NO$	$C_{22}H_{18}F_{16}I_2N_2O_2$
Formula weight	600.12	600.12	576.99	677.01	900.18
Temperature (K)	120.0(1)	170.0(1)	170.0(1)	170.0(1)	120.0(1)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions: a (Å)	10.9762(2)	7.4942(2)	8.03060(10)	8.15770(10)	5.8549(3)
b (Å)	6.97220(10)	7.8268(2)	9.4596(2)	9.47430(10)	8.8666(5)
c (Å)	12.9857(3)	9.7134(2)	11.9618(2)	14.3552(2)	14.3166(9)
α (°)	90	81.2810(14)	72.1708(10)	73.1344(9)	91.878(5)
β (°)	96.298(2)	82.5773(12)	83.0254(9)	78.8453(8)	99.217(5)
γ (°)	90	62.6685(11)	71.2714(8)	71.3129(9)	102.399(5)
Volume (Å^3)	987.78(3)	499.14(2)	818.98(3)	999.60(2)	714.77(7)
Z	4	1	2	2	1
Density (calculated) (mg m^{-3})	2.018	1.996	2.340	2.249	2.091
Absorption coefficient (mm^{-1})	3.233	3.199	3.921	3.258	2.330
F(000)	572	286	536	632	430
Crystal size (mm^3)	0.168×0.091×0.046	0.168×0.108×0.093	0.585×0.512×0.406	0.588×0.342×0.235	0.305×0.244×0.150
θ range for data collection (°)	3.157 to 25.246	2.946 to 27.882	2.532 to 27.862	2.341 to 27.865	3.601 to 25.246
Reflections collected	3737	8948	14913	18728	4606
[R(int)]	[0.0227]	[0.0282]	[0.0263]	[0.0352]	[0.0199]
Reflections [$I > 2\sigma(I)$]	1622	2151	3564	4145	2441
Data completeness (%)	99.9	99.8	99.0	99.8	99.7
Data/restraints/ parameters	1790/0/120	2337/0/120	3820/686/321	4710/914/429	2572/1/201
Goodness-of-fit on F^2	1.048	1.045	1.105	1.027	1.070
Final R indices	R_1 = 0.0261,	R_1 = 0.0225,	R_1 = 0.0212,	R_1 = 0.0266,	R_1 = 0.0326,
[$I > 2\sigma(I)$]	wR_2 = 0.0499	wR_2 = 0.0455	wR_2 = 0.0484	wR_2 = 0.0577	wR_2 = 0.0796
Final R indices	R_1 = 0.0302,	R_1 = 0.0257,	R_1 = 0.0235,	R_1 = 0.0317,	R_1 = 0.0345,
[all data]	wR_2 = 0.0528	wR_2 = 0.0464	wR_2 = 0.0494	wR_2 = 0.0599	wR_2 = 0.0809
Largest diff. peak/hole (e Å^{-3})	1.151/−0.549	0.417/−0.372	0.631/−0.595	1.213/−0.545	2.139/−0.701

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Table S5. Crystal data and X-Ray experimental details for **8•DI2** and **8•DI6**

Complex	**8•DI2**	**8•DI6**
CCDC Number	1554424	1554425
Empirical formula	$C_{18}H_{22}F_4I_2N_2O_2$	$C_{30}H_{33}F_{12}I_2N_3O_3$
Formula weight	628.18	965.39
Temperature (K)	170.0(1)	123.0(1)
Crystal system	Monoclinic	Monoclinic
Space group	*I*2/*a*	$P2_1/c$
Unit cell dimensions: *a* (Å)	10.970(2)	12.1296(3)
b (Å)	14.514(3)	13.6330(3)
c (Å)	14.587(3)	22.6865(5)
α (°)	90	90
β (°)	101.98(3)	99.849(2)
γ (°)	90	90
Volume (Å^3)	2272.0(8)	3696.21(15)
Z	4	4
Density (calculated) (mg m^{-3})	1.836	1.735
Absorption coefficient (mm^{-1})	2.815	1.796
F(000)	1208	1888
Crystal size (mm^3)	0.12×0.10×0.10	0.19×0.18×0.18
θ range for data collection (°)	2.001 to 25.248	3.086 to 25.250
Reflections collected [*R*(int)]	5517 [0.0342]	12232 [0.0378]
Reflections [$I > 2\sigma(I)$]	1454	4955
Data completeness (%)	99.6	99.6
Data/restraints/ parameters	2049/4/136	6666/0/422
Goodness-of-fit on F^2	1.058	1.006
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0580, wR_2 = 0.1477	R_1 = 0.0412, wR_2 = 0.0731
Final *R* indices [all data]	R_1 = 0.0833, wR_2 = 0.1628	R_1 = 0.0656, wR_2 = 0.0835
Largest diff. peak/hole (*e* Å^{-3})	2.061/−1.321	0.676/−0.722

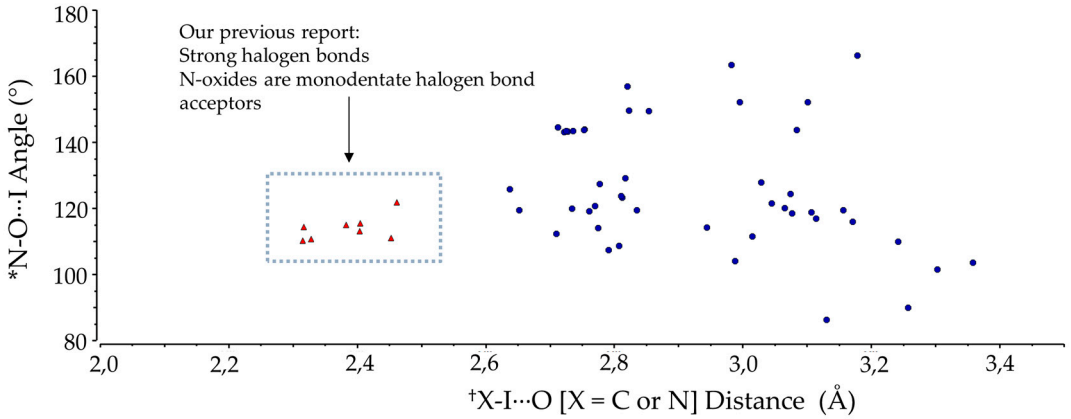

Figure S1 Scatter plot of N-O···I angles vs. I···O distances in *N*-oxide oxygens functioning as halogen bond acceptors, as found in CCDC Notes: * N is *N*-oxide nitrogen atom and †X was selected to be either C or N in X-I halogen bond donor. Search was performed using CCDC 2017, version V5.38, and no limitations were imposed on 3D parameters, N-O···I angles and I···O distances.

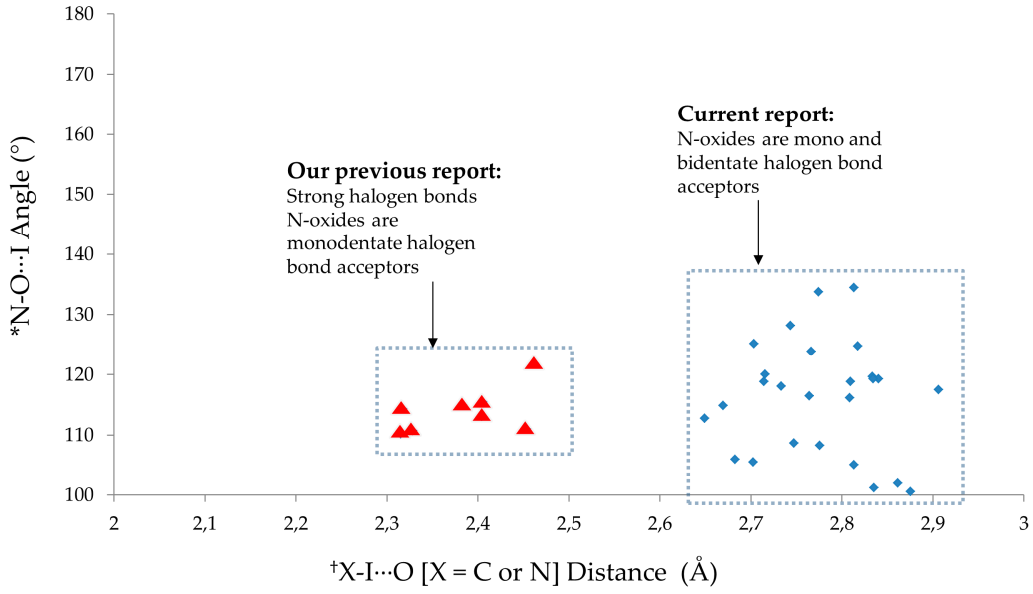

Figure S2 Scatter plot N-O···I angles *vs* I···O distances comparison of our previous and current results in *N*-oxide oxygens functioning as halogen bond acceptors.
Notes: * N is *N*-oxide nitrogen atom and † X was selected to be either C or N in X-I halogen bond donor.