Article

Aromatic diamines as halogen bond acceptors

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Table of Content

Item	Page
Figures S1–S5 (ORTEP representations of the formula units of the prepared compounds)	1
Figures S6–S10 (PXRD patterns of the prepared compounds)	3
Figures S11–S15 (DSC curves of the prepared compounds)	6
Table S1 Masses of reactants and volumes of solvents for successful crystallization experiments.	8
Table S2 (Crystallographic data)	9
Total electron energies and Cartesian coordinates for optimised structures	10

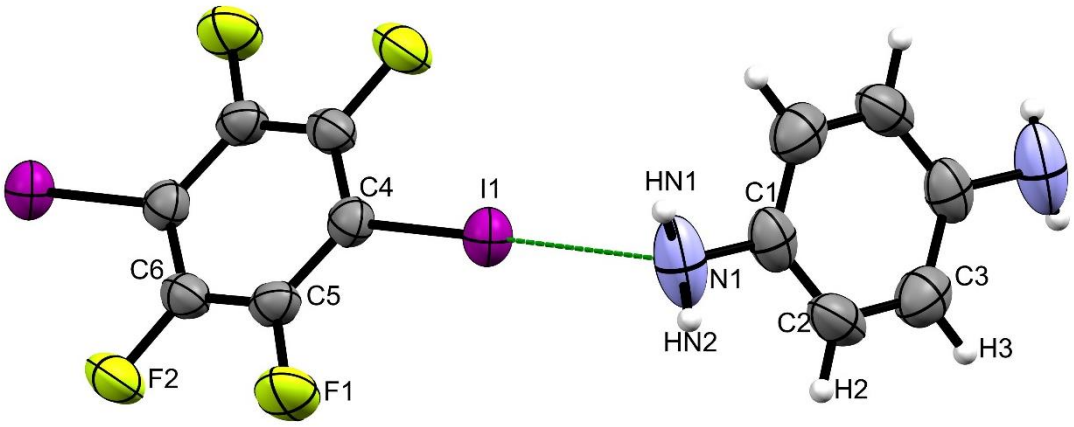

Figure S1. Molecular structure of (**pphda**)(**14tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

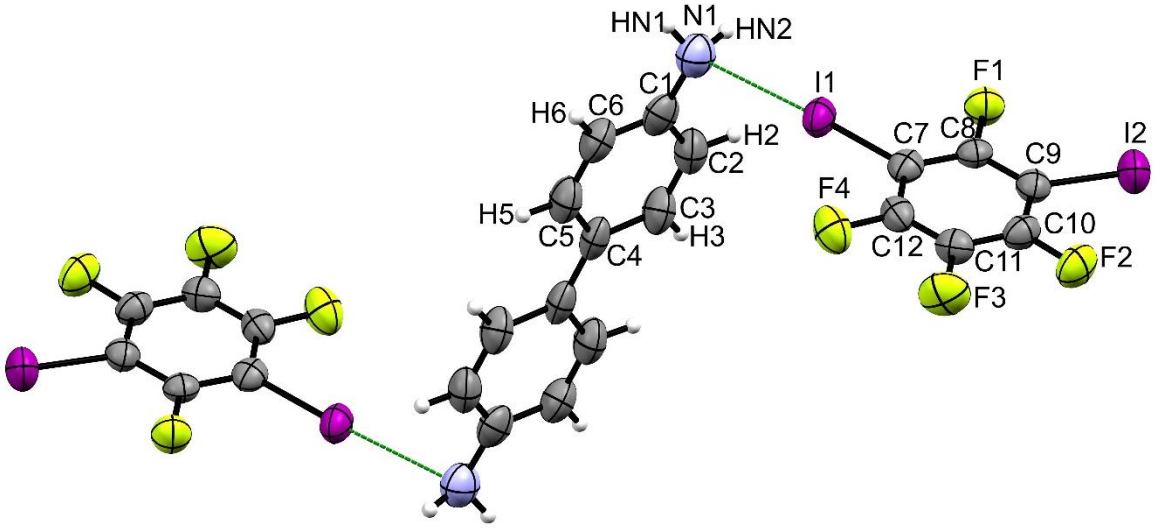

Figure S2. Molecular structure of (**bnzd**)(**13tfib**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

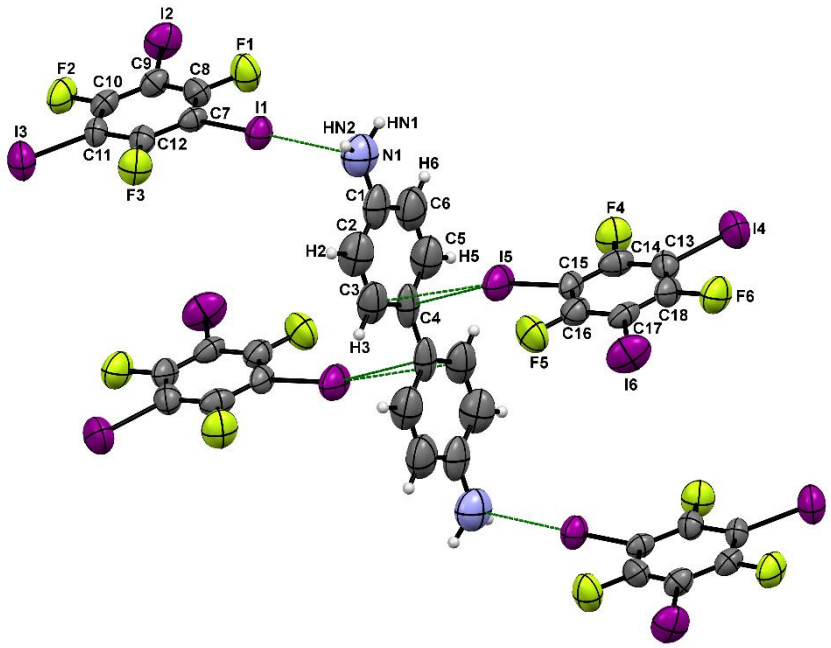

Figure S3. Molecular structure of **(bnzd)(135tfib)**$_4$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

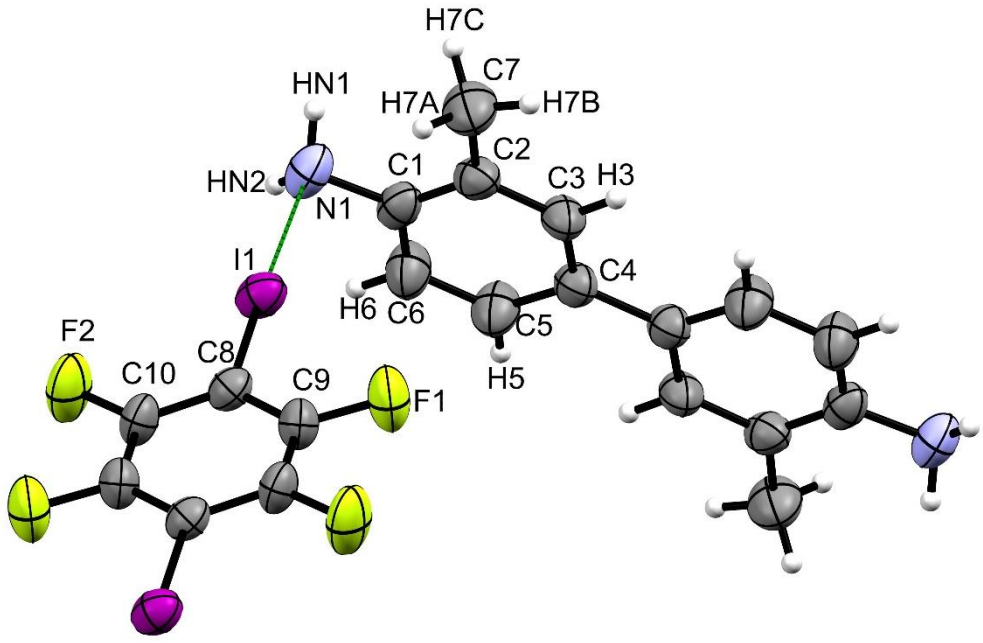

Figure S4. Molecular structure of **(otol)(14tfib)** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

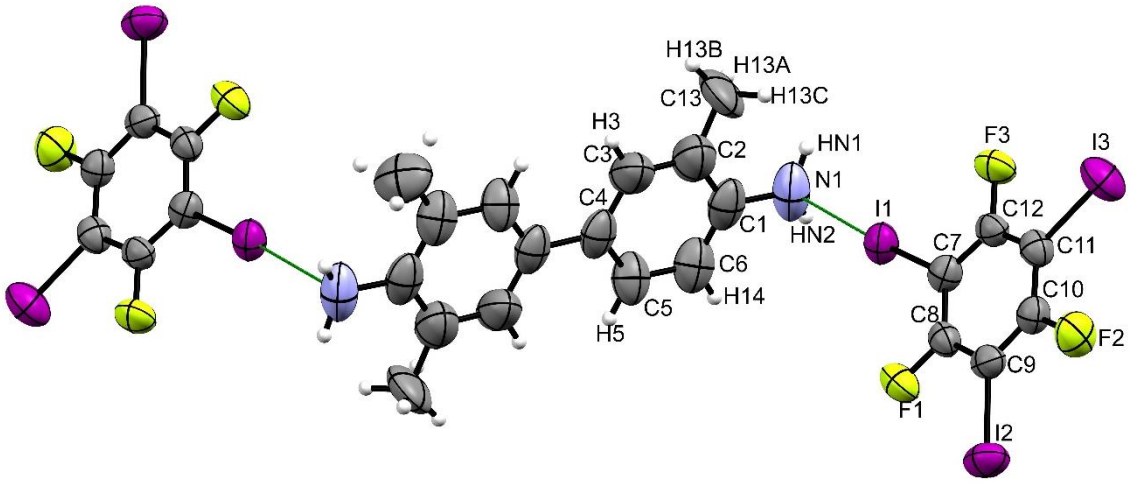

Figure S5. Molecular structure of (**otol**)(**135tfib**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

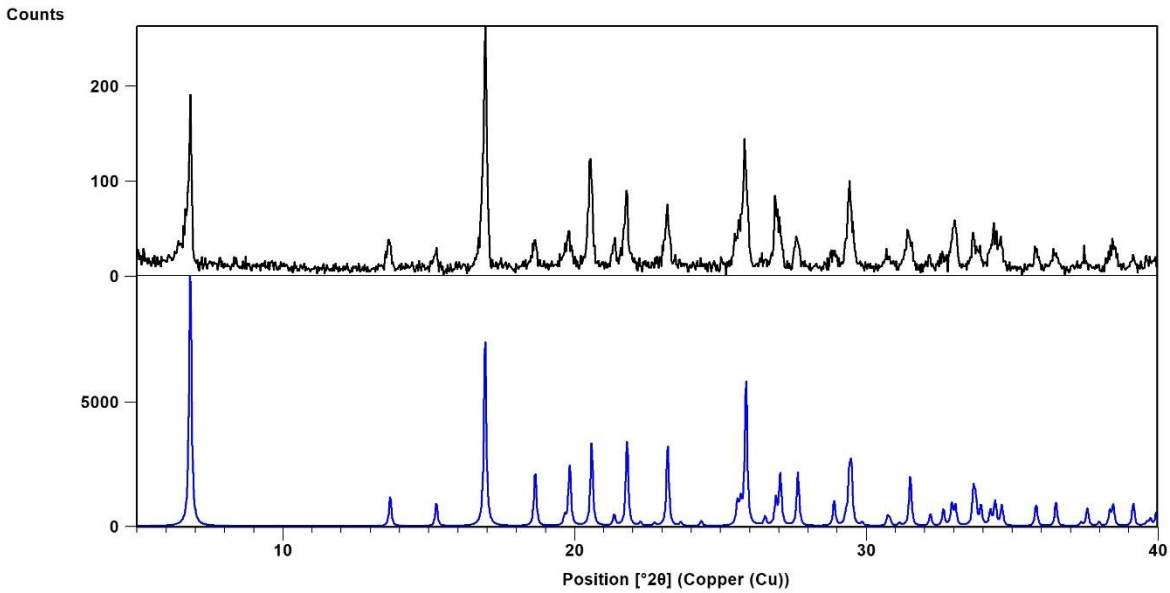

Figure S6. Measured (black) and calculated (blue) PXRD patterns of (**pphda**)(**14tfib**).

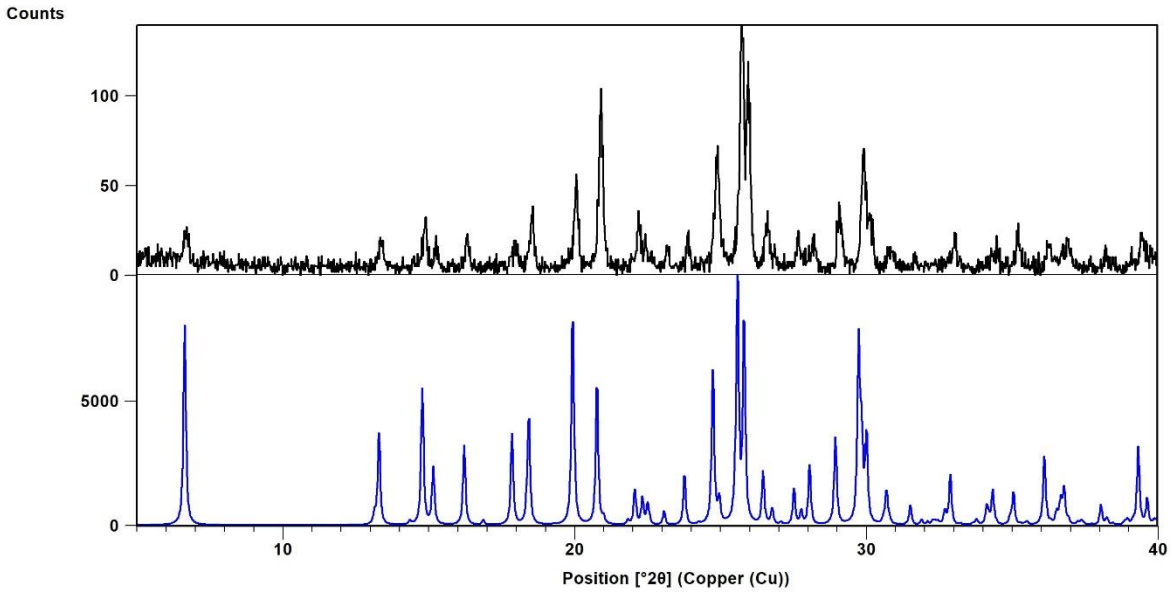

Figure S7. Measured (black) and calculated (blue) PXRD patterns of (**bnzd**)(**13tfib**)$_2$.

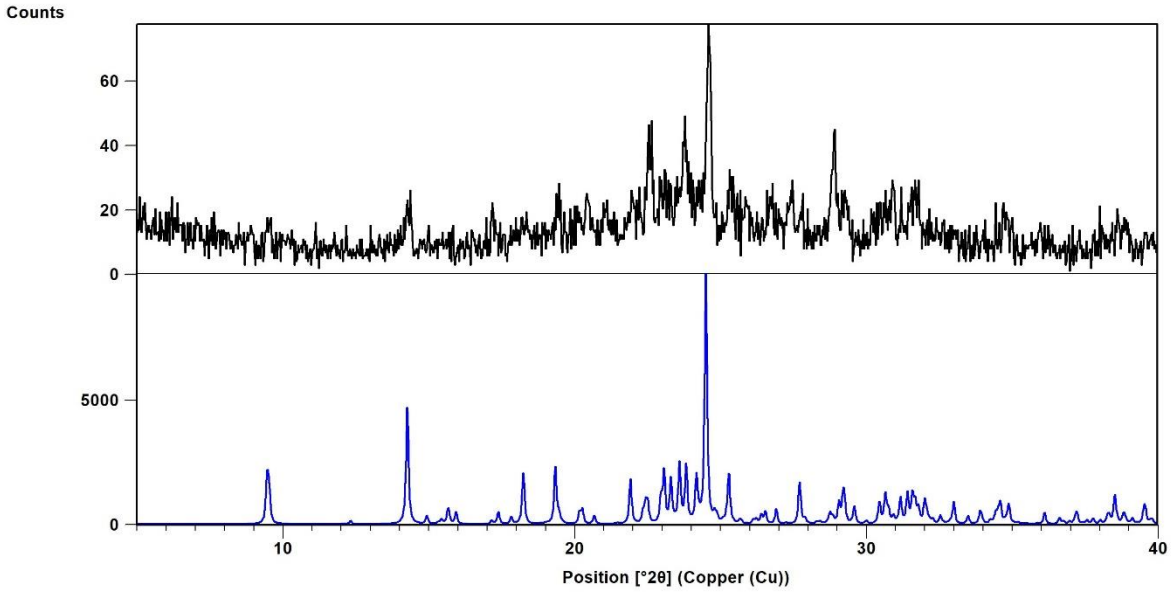

Figure S8. Measured (black) and calculated (blue) PXRD patterns of (**bnzd**)(**135tfib**)$_4$.

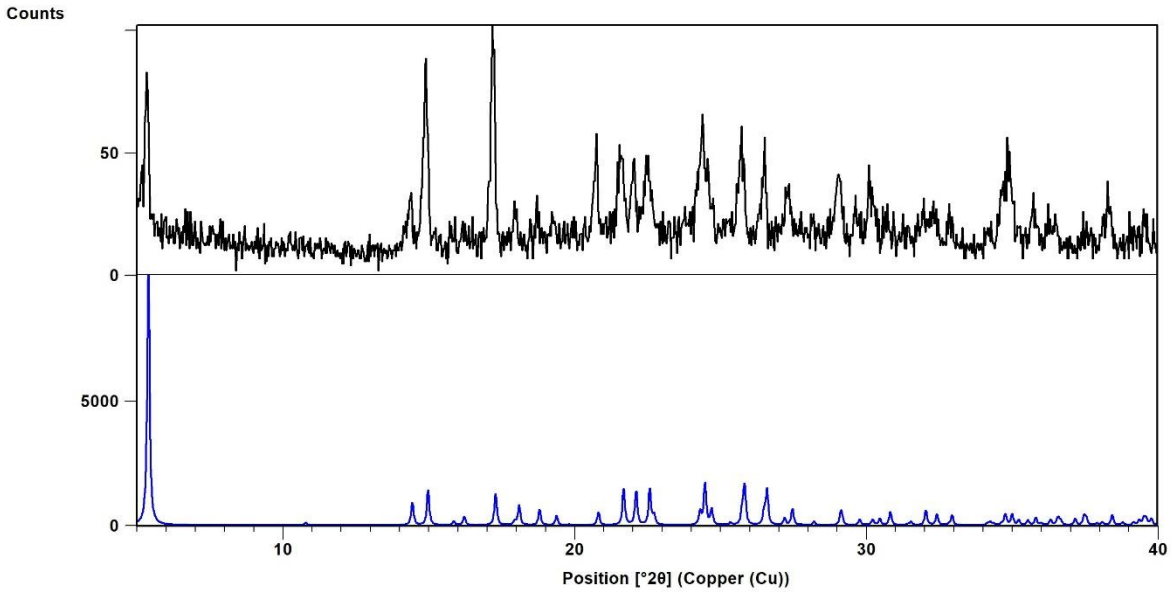

Figure S9. Measured (black) and calculated (blue) PXRD patterns of **(otol)(14tfib)**.

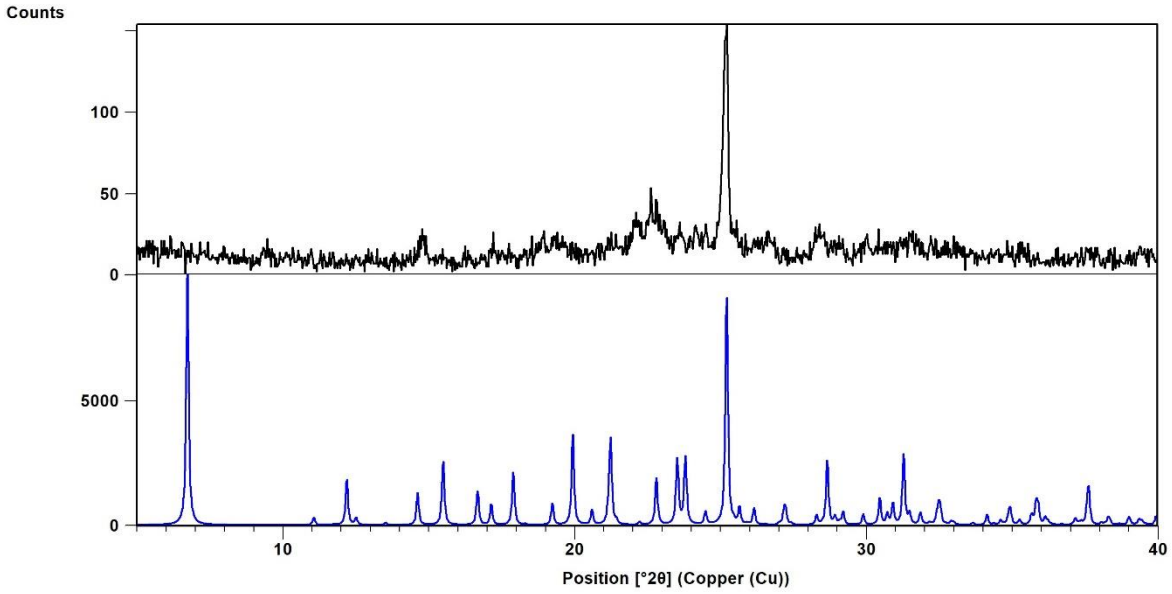

Figure S10. Measured (black) and calculated (blue) PXRD patterns of (**otol**)(**135tfib**)$_2$.

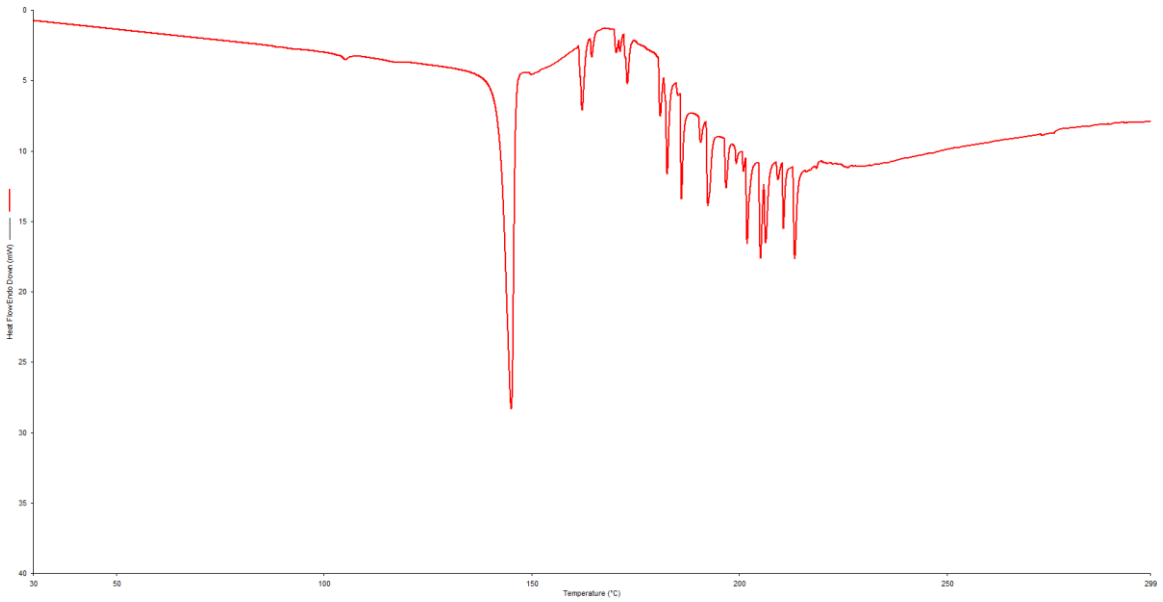

Figure S11. DSC thermogram of product of solution synthesis of (**pphda**)(**14tfib**).

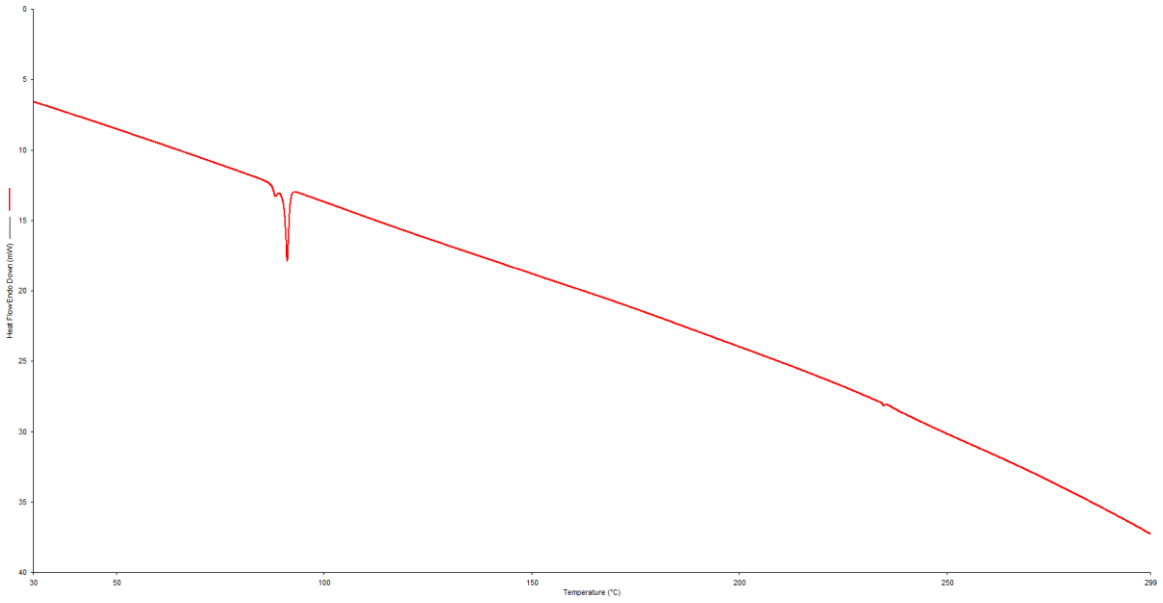

Figure S12. DSC thermogram of product of solution synthesis of (**bnzd**)(**13tfib**)$_2$.

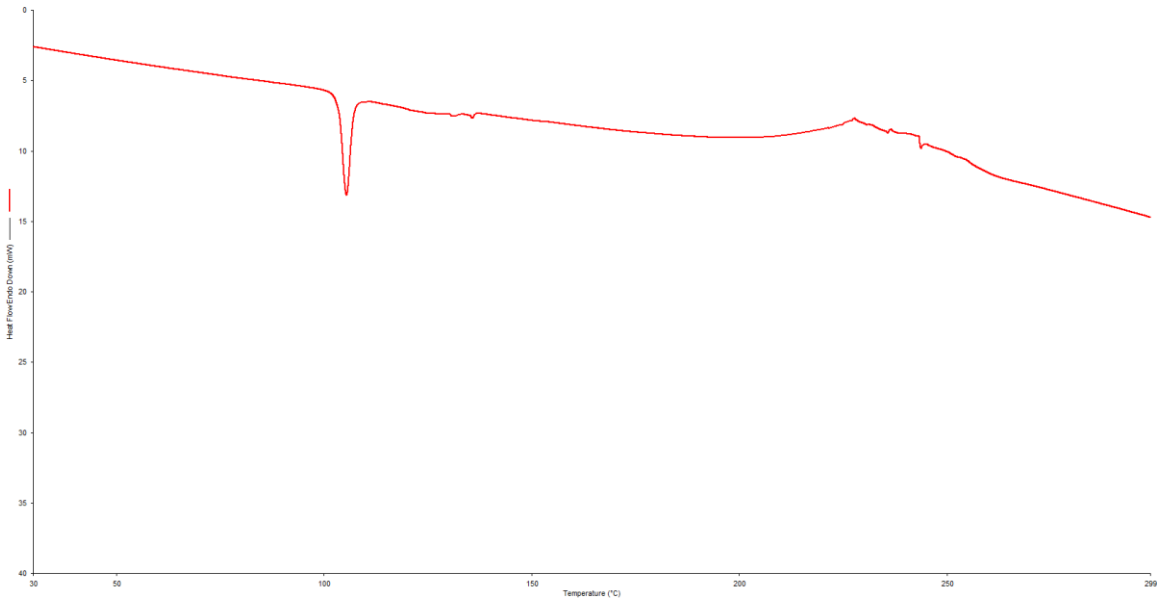

Figure S13. DSC thermogram of product of solution synthesis of (**bnzd**)(**135tfib**)$_4$.

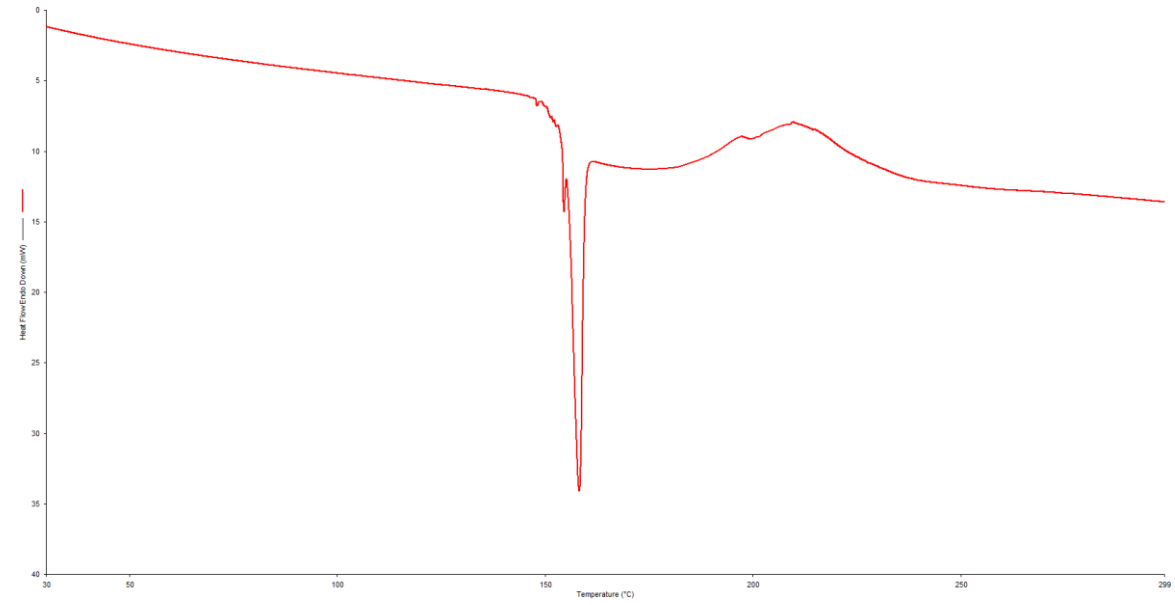

Figure S14. DSC thermogram of product of solution synthesis of **(otol)(14tfib)**.

Figure S15. DSC thermogram of (**otol**)(**135tfib**)$_2$.

Table S1. Masses of reactants and volumes of solvents for successful crystallization experiments.

Reactants		Molar ratio A : D	*m* (A) / mg	*m* (D) / mg	Solvent (L)	*V*(L) / mL
A	D					
otol	**14tfib**	1 : 1	10	20	EtOH	2
otol	**135tfib**	1 : 2	10	40	EtOH	10
bnzd	**13tfib**	1 : 2	10	40	EtOH	3
bnzd	**135tfib**	1 : 2	10	50	EtOH	3
pphda	**14tfib**	1 : 1	10	35	EtOH/Me_2CO	3

Table S2. An overview and crystallographic data of the prepared compounds.

	(pphda)(14tfib)	**(bnzd)(13tfib)**$_2$	**(bnzd)(135tfib)**$_4$	**(otol)(14tfib)**	**(otol)(135tfib)**$_2$
Molecular formula	$C_{12}H_8F_4I_2N_2$	$C_{24}H_{12}F_8I_4N_2$	$C_{30}H_{20}F_{12}I_{12}N_2$	$C_{20}H_{20}F_4I_2N_2$	$C_{26}H_{16}F_6I_6N_2$
M_r	510.00	987.96	2159.28	618.18	1231.81
Crystal system	triclinic	orthorhombic	triclinic	triclinic	monoclinic
Space group	P –1	P bca	P –1	P –1	P $2_1/c$
Crystal data:					
a / Å	4.6046(3)	8.5466(5)	9.4338(12)	5.0079(3)	7.5646(3)
b / Å	6.1794(5)	11.9758(7)	11.7698(15)	6.1910(3)	26.2421(13)
c / Å	13.2376(11)	26.6168(9)	11.9237(11)	16.5464(8)	8.4074(4)
α / °	81.193(7)	90	75.793(9)	94.147(4)	90
β / °	80.366(6)	90	86.652(9)	96.507(5)	94.025(4)
γ / °	82.247(6)	90	82.035(8)	96.482(5)	90
V / Å^3	364.65(5)	2722.3(2)	1270.7(3)	504.55(5)	1664.84(13)
Z	1	4	1	1	2
D_{calc} / g cm^{-3}	2.322	2.409	2.905	2.021	2.457
λ(Mo$K\alpha$) / Å	0.71073	0.71073	0.71073	0.71073	0.71073
T / K	295	295	295	295	295
Crystal size / mm^3	0.28 x 0.24 x 0.16	0.26 x 0.15 x 0.08	0.30 x 0.12 x 0.10	0.22 x 0.22 x 0.18	0.18 x 0.18 x 0.14
μ / mm^{-1}	4.346	4.648	7.385	3.160	5.651
F(000)	236	1816	986	292	1116
Refl. collected/unique	3031 / 1576	16542 / 2657	7917 / 4425	4809 / 2188	10315 / 3620
Data/restraints / parameters	99	179	286	134	200
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.391; –1.074	0.565; –0.747	2.168; –1.542	0.501; –0.705	0.710; –0.968
$R[F^2 > 4\sigma(F^2)]$	0.0284	0.0372	0.0597	0.0278	0.0413
w$R(F^2)$	0.0661	0.0846	0.1710	0.0724	0.1050
Goodness-of-fit, S	1.083	1.095	1.025	1.035	1.043

Total electron energies and Cartesian coordinates for optimised structures:

Aniline

$E = -287.78568793$ a.u.

1	C	0	0.935599	0.000005	−0.007480
2	C	0	0.219775	1.203289	−0.004196
3	C	0	−1.167913	1.197851	0.003296
4	C	0	−1.875425	0.000000	0.006870
5	C	0	−1.167905	−1.197856	0.003292
6	C	0	0.219776	−1.203289	−0.004195
7	H	0	0.758374	2.144371	−0.011304
8	H	0	−1.700290	2.141251	0.007302
9	H	0	−2.957291	−0.000010	0.013265
10	H	0	−1.700289	−2.141252	0.007294
11	H	0	0.758387	−2.144364	−0.011292
12	N	0	2.328248	0.000000	−0.073409
13	H	0	2.779966	0.836168	0.261529
14	H	0	2.779961	−0.836167	0.261542

Methylamine

$E = -95.90249789$ a.u.

1	N	0	−0.749282	−0.000001	−0.120150
2	H	0	−1.153826	−0.813506	0.327764
3	H	0	−1.153822	0.813506	0.327765
4	C	0	0.706511	−0.000001	0.017425
5	H	0	1.116606	−0.878107	−0.485304
6	H	0	1.116590	0.878184	−0.485179
7	H	0	1.080360	−0.000070	1.051459

Iodopentafluorobenzene

E = −1025.91139651 a.u.

1	C	0	0.209838	−0.000111	−0.000074
2	C	0	−0.503142	1.194287	−0.000110
3	C	0	−1.891350	1.201319	0.000048
4	C	0	−2.587057	−0.000091	0.000134
5	C	0	−1.891563	−1.201511	0.000027
6	C	0	−0.503205	−1.194260	−0.000146
7	F	0	0.129251	2.368821	−0.000256
8	F	0	−2.559275	2.354530	0.000047
9	F	0	−3.917117	0.000390	0.000074
10	F	0	−2.559186	−2.354740	0.000079
11	F	0	0.129154	−2.368926	−0.000268
12	I	0	2.301763	0.000029	0.000069

Aniline dimer

E = −575.46220950 a.u.

1	N	0	1.047720	2.003497	0.205657
2	C	0	1.819415	0.858136	0.033235
3	C	0	3.212068	0.907220	0.182737
4	C	0	3.978702	−0.243629	0.064498
5	C	0	3.381502	−1.471361	−0.202532
6	C	0	1.998591	−1.524972	−0.350323
7	C	0	1.222004	−0.380967	−0.236147
8	H	0	1.536113	2.874535	0.072773
9	H	0	0.128993	2.008278	−0.217181
10	H	0	3.691254	1.856522	0.396362
11	H	0	5.053743	−0.177913	0.182068
12	H	0	3.981362	−2.367235	−0.294495
13	H	0	1.511881	−2.470285	−0.558453
14	H	0	0.148020	−0.445366	−0.347800
15	N	0	−2.117948	2.188747	−0.425500
16	C	0	−2.297486	0.827506	−0.134999
17	C	0	−2.555684	−0.089371	−1.157454
18	C	0	−2.628373	−1.447803	−0.879026
19	C	0	−2.446675	−1.916428	0.417654
20	C	0	−2.192463	−1.004078	1.436376
21	C	0	−2.117617	0.355084	1.167855
22	H	0	−2.566670	2.502905	−1.272844
23	H	0	−2.311102	2.811784	0.344687
24	H	0	−2.682223	0.263547	−2.174608
25	H	0	−2.823186	−2.143906	−1.685263
26	H	0	−2.497063	−2.975895	0.630025
27	H	0	−2.037915	−1.352485	2.449656
28	H	0	−1.885516	1.053779	1.962718

Aniline_iodopentafluorobenzene

E = −1313.64758258 a.u.

1	I	0	−0.497474	−0.619114	−0.580661
2	F	0	2.048077	−2.373829	0.383395
3	F	0	1.147372	2.157433	−0.670610
4	C	0	1.514481	−0.128781	−0.161208
5	C	0	1.970397	1.179127	−0.280061
6	C	0	2.422896	−1.097387	0.249313
7	F	0	3.703613	2.779290	−0.119772
8	F	0	4.598875	−1.725289	0.928464
9	C	0	4.177129	0.533531	0.409949
10	C	0	3.743689	−0.778980	0.534709
11	C	0	3.287335	1.516852	0.000615
12	C	0	−5.136237	1.778769	0.192053
13	H	0	−5.389350	2.778474	−0.138002
14	C	0	−4.471511	−0.785931	1.017986
15	H	0	−4.202814	−1.783436	1.346302
16	C	0	−5.487813	1.356819	1.469786
17	N	0	−3.378658	−1.204678	−1.114890
18	H	0	−3.492401	−1.010087	−2.099282
19	H	0	−3.491259	−2.190859	−0.928955
20	C	0	−4.458037	0.929541	−0.671509
21	H	0	−4.177573	1.271239	−1.661184
22	C	0	−4.123569	−0.363890	−0.266385
23	H	0	−6.016140	2.021391	2.140257
24	C	0	−5.149582	0.070175	1.875045
25	H	0	−5.413859	−0.273154	2.867382
26	F	0	5.442624	0.848302	0.681963

Methylamine dimer

E = −191.81295444 a.u.

1	N	0	1.405064	−0.612568	−0.427370
2	H	0	1.982661	−1.444117	−0.396004
3	H	0	0.517481	−0.837375	0.017212
4	N	0	−1.659380	−0.621527	0.334857
5	H	0	−2.218699	−0.675898	1.177404
6	H	0	−2.019829	−1.317211	−0.307565
7	C	0	−1.728531	0.717291	−0.259777
8	H	0	−1.355969	1.446985	0.460905
9	H	0	−1.069223	0.751787	−1.127880
10	H	0	−2.733298	1.030072	−0.571390
11	C	0	2.058180	0.492085	0.271553
12	H	0	3.000944	0.737816	−0.222630
13	H	0	1.423845	1.379264	0.211933
14	H	0	2.274403	0.311091	1.334953

Methylamine_iodopentafluorobenzene

E = −1121.82761655 a.u.

1	I	0	−1.666467	−0.146556	−0.131432
2	F	0	0.661680	−2.394498	0.034305
3	F	0	0.425028	2.336359	−0.104682
4	C	0	0.453909	−0.033698	−0.038484
5	C	0	1.112589	1.189651	−0.044090
6	C	0	1.231564	−1.183436	0.025872
7	F	0	3.108095	2.459843	0.005089
8	F	0	3.343395	−2.243536	0.143837
9	C	0	3.252487	0.109592	0.075736
10	C	0	2.617311	−1.124311	0.082878
11	C	0	2.497258	1.272154	0.012070
12	N	0	−4.517990	−0.285436	−0.228251

13	H	0	−4.804661	−0.093458	−1.180734
14	H	0	−4.781914	−1.240855	−0.018907
15	F	0	4.582425	0.177906	0.129570
16	C	0	−5.125490	0.658554	0.715505
17	H	0	−4.769327	0.434813	1.721309
18	H	0	−4.797708	1.668693	0.469257
19	H	0	−6.221063	0.640620	0.722749