CrystEngComm

Supporting Information

Just at the limit: binding studies with neutral brominated terphenyl-derived halogen bond donors

Julian Stoesser[a], Elric Engelage[a], Debora Belmonte[a] and Stefan M. Huber*[a]

a) Department of Chemistry and Biochemistry, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany. E-mail: stefan.m.huber@rub.de.

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A.) Synthesis and Experimental Data

A.1) General Information

A.1.1) Chemicals

All the used chemicals were obtained from *ABCR*, *Alfa Aesar*, *Carbolutions*, *Fluorochem*, *Merck*/*Sigma Aldrich* or *VWR*. Commercially available reagents and starting materials were unless mentioned otherwise, used without further purification. Solvents that were used in moisture sensitive experiments were taken from a solvent drying system by *M.Braun* (type: *MB SPS-800*) and stored over molecular sieve. Methanol, acetonitrile, and chloroform were bought in peptide grade quality and also dried over molecular sieves. Other solvents were bought in technical grade quality and used after single distillation.

For reactions including oxygen or moisture sensitive reagents, glassware was dried under high-vacuum conditions (10^{-2} mbar) and procedures were carried out under an argon atmosphere. Reagents were injected via a septum or added under argon counterflow.

A.1.2) Appliances and materials

Thin layer chromatography (TLC) was performed on plates from *Merck* (silica gel 60, F254). Detection of the substances was obtained by fluorescence detection under UV light (wavelength λ = 254 nm). The corresponding R_f values and solvents used as eluents are listed in the experimental part. Column chromatographies were performed with silica gel (grain size 0.04-0.063 cm, *Merck, Si60*). The used eluent relations are listed with the respective experiments.

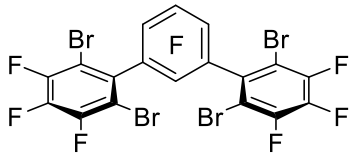
^{19}F and ^{13}C-Nuclear magnetic resonance spectra (NMR spectra) were recorded on either Bruker Avance III 300, DPX 250 or DRX 400 spectrometers at 25°C. All shift values are in ppm and all coupling constants (J) are printed in Hertz (Hz) with their multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet).
GC/MS spectra were measured on an Agilent 7820gc/5977sd GC/MS System using H_2 as carrier gas equipped with an Agilent HP5MS.

Infrared spectra were measured on a Shimadzu FTIR-8400s spectrometer equipped with a Specac Quest ATR unit.

Elemental analyses were performed on a *vario MICRO cube* from Elementar Analysensysteme GmbH.

A.2) Synthesis of the halogen bond donors

A.2.1) Bis-1,3-(2,6-dibromotrifluorophenyl)-tetrafluorobenzene (1,3-Ter^{4Br})



A 100 ml round bottom flask was charged with 30 ml (339.84 mmol, 139.41 eq) of trifluoromethanesulfonic acid and cooled to 0 °C. Then 1.0 g (2.44 mmol, 1 eq) bis-1,3-(3,4,5-trifluorophenyl)-tetrafluorobenzene was added. Over the course of 1 hour 3.47 g (19.50 mmol, 8 eq) N-bromosuccinimide was added in portions and the reaction mixture turned subsequently dark brown. The suspension was stirred overnight and allowed to warm to room temperature. After that, the reaction mixture was poured onto crushed ice and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were neutralized with saturated $NaHCO_3$-solution, washed with saturated $Na_2S_2O_3$ and NaCl-solution and dried over $MgSO_4$. After removing the solvent under reduced pressure, a yellow residue was obtained. This residue was purified by column chromatography using petroleum ether as eluent. Thus 2,2'',6,6''-Tetrabromodecafluoro-1,3-terphenyl was obtained as a white crystalline solid in 40% (715 mg, 0.98 mmol) yield.

^{19}F NMR (250 MHz, Chloroform-*d*)

δ = -115.63 (d, *J* = 10.8 Hz, 1F), -120.91 (d, *J* = 21.1 Hz, 4F), -129.17 (d, *J* = 22.2 Hz, 2F), -149.74 (t, *J* = 21.1 Hz, 2F), -161.63 (td, *J* = 22.1, 10.8 Hz, 1F)

^{13}C NMR (63 MHz, Chloroform-*d*)

δ = 152.37 (dtd, J = 249.2, 6.7 ,3.6 Hz), 149.32 (dddd, J= 255.6, 11.5 8.6 ,5.9 Hz),
148.66 (ddd,*J* = 252.5, 11.7, 3.8 Hz), 141.28 (dt,*J* = 262.4, 16.9 Hz),
137.90 (dtd, *J* = 253.0, 15.7, 5.3 Hz), 126.30 (d, *J* = 3.2 Hz), 114.36-112.09 (m),
110.16-108.03 (m).

IR-Peaks [cm^{-1}]: 461.0; 499.7; 582.5; 601.8; 642.3; 682.8; 721.4; 729.1; 744.5; 758.0; 877.6; 993.3;1074.4; 1107.1; 1124.5; 1226.7; 1259.5; 1330.9; 1340.5; 1411.9; 1475.5; 1585.5; 1602.8; 1645.3.

R_f-value (Petrol ether (40-60°)): 0.65

EI-MS:

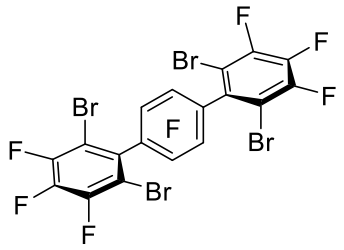
m/z [+] calc. = 725.8 [M^+] found = 725.8 [M^+]

Elemental Analysis:

calc. C = 29.79 found = 30.35

Melting point: 163.5 °C

A.2.2) Bis-1,4-(2,6-dibromotrifluorophenyl)-tetrafluorobenzene (1,4-Ter^{4Br})



For this synthesis, the same procedure as for 1,3-Ter^{4Br} was used except 1.0 g (2.44 mmol, 1 eq) of bis-1,4-(3,4,5-trifluorophenyl)-tetrafluorobenzene was used. This way 2,2",6,6"-Tetrabromodecafluoro-1,4-terphenyl was obtained as a white crystalline solid in 18% (309 mg, 0.43 mmol) yield.

^{19}F NMR (250 MHz, Chloroform-*d*)

δ = -120.74 (d, *J* = 21.1 Hz, 4F), -138.27 (s, 4F),-149.47 (t, *J* = 21.1 Hz, 2F).

^{13}C NMR (63 MHz, Chloroform-*d*)

δ = 148.58 (ddd, *J* = 252.7, 11.7, 3.8 Hz), 146.12-141.09 (m), 141.40 (td, *J* = 262.6, 16.8 Hz), 126.04 (d, *J* = 4.4 Hz), 118.88 (t, *J* = 10.4 Hz), 109.36-107.25 (m).

IR-Peaks [cm^{-1}]: 640.4; 705.9; 746.5; 877.6; 979.8; 995.3; 1068.6; 1080.1; 1226.7; 1234.4; 1251.8; 1263.4; 1329.0; 1338.6; 1354.0; 1363.7; 1410.0; 1471.7; 1510.3; 1583.6; 1602.8

R_f-value (Petrol ether (40-60°)): 0.79

EI-MS:

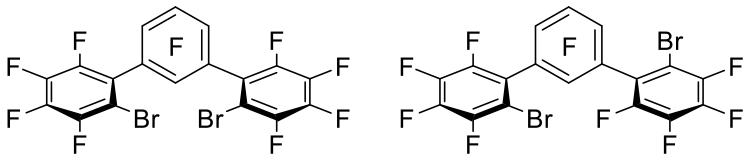
m/z [+] calc. = 725.8 [M^+] found = 725.8 [M^+]

Elemental analysis:

calc. C = 29.79 found = 30.26

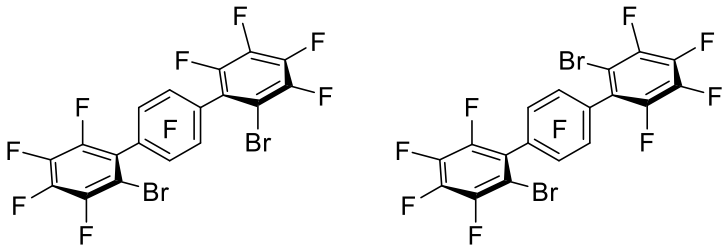
Melting point: 188.3 ° C

A.2.3) *syn*-Bis-1,3-(2-bromotetrafluorophenyl)-tetrafluorobenzene (*syn*-1,3-Ter^{2Br})
anti-Bis-1,3-(2-bromotetrafluorophenyl)-tetrafluorobenzene (*anti*-1,3-Ter^{2Br})



For this synthesis, the same procedure as for 1,3-Ter^{4Br} was used except 1.0 g (2.24 mmol, 1 eq) of bis-1,3-(3,4,5,6-tetrafluorophenyl)-tetrafluorobenzene was used. A mixture of the *syn*-, the *anti*-, the partially and non-brominated compound could be obtained and it was not possible to separate them to perform the needed analysis.

A.2.4) *syn*-Bis-1,4-(2-bromotetrafluorophenyl)-tetrafluorobenzene (*syn*-1,4-Ter^{2Br})
anti-Bis-1,4-(2-bromotetrafluorophenyl)-tetrafluorobenzene (*anti*-1,4-Ter^{2Br})



For this synthesis, the same procedure as for 1,3-Ter^{4Br} was used except 1.0 g (2.24 mmol, 1 eq) of bis-1,4-(3,4,5,6-tetrafluorophenyl)-tetrafluorobenzene was used. A mixture of *syn*- and *anti*- Bis-1,**4**-(2-bromotetrafluorophenyl)-tetrafluorobenzene was obtained as a white powder in 62% (839 mg, 1,39 mmol) yield.

"presumably" (based on iodinated analogue) *syn*-1,4-Ter^{2Br}:

^{19}F NMR (250 MHz, Chloroform-*d*)

δ =-126.43 (ddd, *J* = 21.9, 10.0, 3.8 Hz), -133.38 (dddd, *J* = 21.7, 7.8, 4.3, 2.1 Hz), -137.07 (t, *J* = 1.7 Hz), -148.94 (ddd, *J* = 21.9, 20.1, 4.5 Hz), -153.65 (ddd, *J* = 21.7, 20.2, 3.8 Hz).

"presumably" (based on the iodinated analogue) *anti*-1,4-Ter^{2Br}:

^{19}F NMR (250 MHz, Chloroform-*d*)

δ = -126.39 (ddd, *J* = 21.8, 9.7, 3.8 Hz), -133.25 (dddd, *J* = 23.7, 9.4, 4.3, 2.1 Hz), -137.00 (t, *J* = 1.7 Hz), -148.94 (ddd, J = 21.7, 20.1, 4 5 Hz), -153.53 (ddd, *J* = 21.6,20.2, 3.8 Hz).

The spectra of the known iodinated analogues show that the signals of *syn*-1,4-Ter^{2I} are further upfield-shifted than those of *anti*-1,4-Ter^{2I}. Based on this, the spectra were assigned to the isomers.

^{13}C NMR (63 MHz, Chloroform-*d*)

δ = 148.59-147.18 (m), 146.95-145.32 (m), 144.41-143.34 (m), 142.83-141.14 (m), 139.99 (ddd, *J* = 17.2, 12.8, 4.1 Hz), 138.22 (t, *J* = 15.2 Hz), 115.53-112.04 (m), 108.26-106.22 (m).

Due to the overlapping peaks of *syn*- and *anti*-1,4-Ter^{2Br}, no clear pattern can be determined. Because of that, the signals are given as multiplets.

IR-Peaks [cm^{-1}]: 412.8; 707.9; 827.5; 933.5; 979.8; 1053.1; 1085.9; 1114.9; 1128.4; 1257.6; 1292.3; 1375.2; 1437.0; 1456.3; 1473.6; 1485.2; 1496.7; 1521.8; 1631.8.

R_f-value (Petrol ether (40-60°)): 0.73

EI-MS:

m/z [+] calc. = 604 [M^+] found = 604 [M^+]

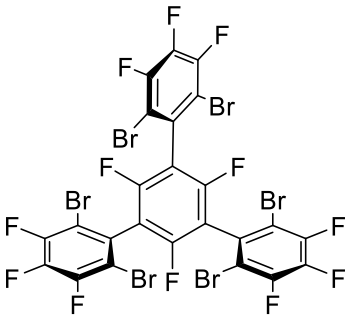
Elemental analysis:

calc. C = 35.80 found = 35.80

Melting point: 177.4 ° C

The melting point refers to the mixture of *syn*- and *anti*- Bis-1,**4**-(2-bromotetrafluorophenyl)-tetrafluorobenzene.

A.2.5) 1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene (Q-Ter^{6Br})



For this synthesis, the same procedure as for 1,3-Ter^{4Br} was used except 2.10 g (4.15 mmol, 1 eq) of 1,3,5-Tris-(3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene were used. 1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene was obtained as white crystalline solid in 51% (486 mg, 0.48 mmol) yield.

^{19}F NMR (250 MHz, Chloroform-*d*)

δ = -107.13(s, 3F), -121.16 (d, *J* = 21.2 Hz, 6F) -150.00 (t, *J* = 21.1 Hz, 3F).

^{13}C NMR (63 MHz, Chloroform-*d*)

δ = 157.29 (dt, *J* = 254.4, 9.3 Hz), 148.49 (ddd, *J* = 252.4, 11.7, 3.8 Hz), 141.06 (dt, *J* = 262.1, 16.9 Hz), 126.58 (d, *J* = 4.5 Hz), 114.10-111.95 (m), 109.85-107.23 (m).

IR-Peaks [cm^{-1}]: 499.6; 609.5; 624.9; 661.6; 731.0; 877.6; 991.4; 1072.4; 1099.4; 1228.7; 1329.0; 1344.4; 1411.9; 1460.1; 1492.9; 1583.5; 1602.8; 1627.9; 1741.7.

R_f-value (Petrol ether (40-60°)): 0.79

EI-MS:

m/z [+] calc. = 995.7 [M^+] found = 955.7 [M^+]

Elemental analysis:

calc. C = 28.95 found = 28.91

B.) Structural Characterization

B.1.) Crystal Structure Determination

Crystal structure determination was carried out on a *Rigaku* XtaLAB mini, equipped with a 600 W Mo micro-fine focus glass sealed tube, graphite monochromator (Mo K_α) and Mercury375R CCD detector or a *Rigaku* Synergy dual source device, with Cu and Mo microfocus sealed tubes (Cu & Mo K_α) using mirror monochromators and a HyPix-6000HE: Hybrid photon counting X-ray detector. Crystals were mounted in *Hampton* CryoLoops using Parabar/Paratone or *GE/Bayer* silicone grease. Data on both systems was recorded and reduced using the CrysalisPro[1] Software. Structures were solved using WinGX[2] in combination with ShelXT[3] and refined with shelXle and ShelXL. Tables for the publication were generated using a modified version of Ciftab. Pictures of the structures were generated with Diamond 4[4].

B.2.) Crystal data

Table S1: Crystal data and structure refinement

Compound	***m*-5^{4Br}**	***p*-5^{4Br}**	***p*-5^{2Br} -*syn***	***p*-5^{2Br} -anti**
Empirical formula	$C_{18}Br_4F_{10}$	$C_{18}Br_4F_{10}$	$C_{18}Br_2F_{12}$	$C_{18}Br_2F_{12}$
CCDC	2183888	2183890	2183892	2183891
Formula weight [g/mol]	725.82	725.82	603.98	604
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	C2/c (15)	$P2_1/n$ (14)	Pbca (61)	P-1 (2)
Lattice parameters [Å]				
a	13.3920(12)	7.7805(5)	7.8665(2)	5.4453(6)
b	10.6012(12)	12.9312(8)	20.2579(3)	7.8772(6)
c	14.1313(13)	16.6717(14)	22.2780(4)	11.0644(9)
α	90	90	90	71.140(7)
β	101.079(9)	94.599(7)	90	86.893(8)
γ	90	90	90	79.296(8)
Density [g/cm^3]	2.449	2.444	2.260	2.273
Crystal size [mm^3]	0.280 x0.184 x 0.143	0.617 x 0.361 x 0.166	0.090 x 0.059 x 0.038	0.485 x 0.259 x 0.124
Volume [Å^3]	1968.8(3)	1972.8(2)	3550.19(12)	441.29(7)
Z	4	4	8	1
Temperature [K]	170(2)	170(2)	169.99(12)	170(2)

Diffraction Device	XtaLAB Mini (ROW)	XtaLAB Mini (ROW)	XtaLAB Synergy, Dualflex, HyPix	XtaLAB Mini (ROW)
Radiation type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)	1.54184 Å (Cu K/ micro-focus sealed X-ray tube)	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F (000)	1352	1352	2288	286
Absorption coefficient [mm^{-1}]	8.273	8.257	7.029	4.719
Absorption correction	Gaussian	Gaussian	Gaussian	Gaussian
Measurement range	2.7 – 26.0	2.9 – 26.0	4.0 – 66.5	2.8 – 26.5
Index range	-16 < h < 14 -9 < k < 13 -17 < l < 11	-9 < h < 9 -15 < k < 15 -24 < l < 24	-9 < h < 9 -24 < k < 23 -26 < l < 13	-6 < h < 6 -9 < k < 9 -13 < l < 13
Measured reflexes	3519	8627	12960	2671
Independent	1935	3876	3127	1811
Observed	1513	3138	2844	1660
R (int)	0.0220	0.0226	0.0341	0.0209
Completeness (%) / theta (°)	99.9 / 25.242	99.9 / 25.242	100.0 / 66.494	99.4 / 25.242
Transmission (min/max)	0.253 / 0.504	0.102 / 0.456	0.709 / 0.943	0.283 / 0.752
R1 (observed/all)	0.0308 / 0.0471	0.0330 / 0.0466	0.0471 / 0.0523	0.0326 / 0.0377
wR2 (observed/all)	0.0675 / 0.0751	0.0756 / 0.0822	0.1051 / 0.1074	0.0818 / 0.0865
GooF = S	1.046	1.021	1.188	1.093
Rest electron density max./min. [$e^{-}/Å^{3}$]	-0.270 / 0.571	-0.539 / 1.093	-0.561 / 0.469	-0.414 / 0.733

Compound	***m*-5^{4Br} TDAI**	***p*-5^{4Br} TDAI**
Empirical formula	$C_{27}H_{18}Br_4F_{10}IN_3$	$C_{27}H_{18}Br_4F_{10}IN_3$
CCDC	2183889	2183893
Formula weight [g/mol]	1020.98	1020.98
Crystal system	Orthorhombic	Monoclinic
Space group	Pbcm (57)	C2/c (15)
Lattice parameters [Å]		
a	20.3907(4)	21.3852(16)
b	7.68010(10)	20.391(2)
c	42.9380(10)	7.5673(6)
α	90	90
β	90	94.255(7)
γ	90	90
Density [g/cm^3]	2.017	2.061
Crystal size [mm^3]	0.256 x 0.074 x 0.057	0.947 x 0.419 x 0.220
Volume [Å^3]	6724.2(2)	3290.7(5)
Z	8	4
Temperature [K]	169.99(10)	170(2)
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix	XtaLAB Mini (ROW)
Radiation type	1.54184 Å (Cu K/ micro-focus sealed X-ray tube)	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F (000)	3872	1936
Absorption coefficient [mm^{-1}]	13.782	5.911
Absorption correction	Gaussian	Gaussian
Measurement range	3.0 – 66.5	2.8 – 26.5
Index range	-24 < h < 24 -4 < k < 9 -50 < l < 50	-26 < h < 26 -25 < k < 25 -9 < l < 9
Measured reflexes	39157	6802
Independent	5995	3416
Observed	5328	2834
R (int)	0.0505	0.0266
Completeness (%) / theta (°)	99.7 / 66.496	99.9 / 25.242
Transmission (min/max)	0.230 / 0.682	0.102 / 0.693
R1 (observed/all)	0.0442 / 0.0501	0.0459 / 0.0573
wR2 (observed/all)	0.1022 / 0.1051	0.1231 / 0.1355
GooF = S	1.145	1.026
Rest electron density max./min. [e$^-$/Å^3]	-0.733 / 0.717	-0,794 / 0.862

Table S2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***m*-5^{4Br}** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	6268(1)	7466(1)	5153(1)	43(1)
F(1)	5141(2)	8848(3)	6466(2)	58(1)
C(1)	4904(3)	8003(4)	4897(3)	32(1)
Br(2)	2388(1)	7997(1)	2663(1)	56(1)
F(2)	3203(2)	9721(3)	6134(2)	65(1)
C(2)	4539(3)	8643(4)	5610(3)	40(1)
F(3)	1982(2)	9340(3)	4428(2)	64(1)
C(3)	3553(4)	9090(4)	5442(3)	45(1)
F(4)	5000	8959(3)	2500	42(1)
C(4)	2931(3)	8890(4)	4571(3)	44(1)
C(5)	3279(3)	8243(4)	3851(3)	37(1)
F(5)	4356(2)	5129(2)	3921(2)	47(1)
C(6)	4276(3)	7788(3)	4005(2)	30(1)
F(6)	5000	3850(3)	2500	49(1)
C(7)	4652(3)	7074(4)	3239(2)	29(1)
C(10)	5000	5106(5)	2500	33(1)
C(9)	4670(3)	5772(4)	3221(3)	34(1)
C(8)	5000	7697(5)	2500	30(1)

Table S3: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***m*-5^{4Br}**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	38(1)	53(1)	36(1)	7(1)	0(1)	1(1)
F(1)	79(2)	62(2)	30(1)	-12(1)	4(1)	-4(2)
C(1)	35(2)	31(2)	30(2)	4(2)	8(2)	-4(2)
Br(2)	36(1)	86(1)	41(1)	-1(1)	0(1)	9(1)
F(2)	88(2)	65(2)	53(2)	-13(1)	40(2)	9(2)
C(2)	56(3)	40(2)	24(2)	-2(2)	12(2)	-8(2)
F(3)	50(2)	82(2)	66(2)	-4(1)	25(1)	22(2)
C(3)	64(3)	41(2)	39(2)	-4(2)	29(2)	2(2)
F(4)	62(2)	30(2)	38(2)	0	21(2)	0

C(4)	40(2)	51(3)	45(3)	4(2)	20(2)	11(2)
C(5)	37(2)	47(3)	27(2)	4(2)	8(2)	4(2)
F(5)	55(2)	45(1)	47(1)	13(1)	21(1)	-5(1)
C(6)	33(2)	32(2)	27(2)	4(1)	10(2)	-2(2)
F(6)	49(2)	30(2)	71(2)	0	19(2)	0
C(7)	28(2)	37(2)	23(2)	1(2)	6(2)	1(2)
C(10)	28(3)	28(3)	43(3)	0	6(2)	0
C(9)	27(2)	44(2)	32(2)	9(2)	7(2)	-3(2)
C(8)	28(3)	36(3)	25(3)	0	3(2)	0

Table S4: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***p*-5^{4Br}** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	11366(1)	4655(1)	4245(1)	34(1)
Br(2)	8682(1)	8778(1)	4073(1)	40(1)
Br(3)	5210(1)	7455(1)	1627(1)	56(1)
Br(4)	4550(1)	3558(1)	2933(1)	54(1)
F(1)	13802(3)	5706(2)	5281(1)	44(1)
F(2)	13928(3)	7689(2)	5679(1)	52(1)
F(3)	11637(4)	9066(2)	5132(1)	53(1)
F(4)	6673(3)	6719(2)	4458(1)	33(1)
F(5)	4162(3)	6138(2)	3545(1)	36(1)
F(6)	8223(3)	5471(2)	1956(1)	40(1)
F(7)	10748(3)	6082(2)	2863(1)	35(1)
F(8)	2287(4)	6550(3)	726(2)	84(1)
F(9)	631(4)	4729(4)	835(2)	98(2)
F(10)	1643(4)	3392(3)	1826(2)	86(1)
C(1)	11409(5)	6056(3)	4491(2)	25(1)
C(2)	12656(5)	6373(3)	4984(2)	30(1)
C(3)	12733(5)	7392(4)	5193(2)	36(1)
C(4)	11548(5)	8089(3)	4914(2)	36(1)
C(5)	10278(5)	7783(3)	4424(2)	30(1)
C(6)	10184(4)	6754(3)	4206(2)	24(1)
C(7)	8803(5)	6409(3)	3697(2)	24(1)
C(8)	7086(5)	6406(3)	3846(2)	26(1)
C(9)	5792(4)	6102(3)	3375(2)	27(1)

C(10)	6118(5)	5770(3)	2726(2)	27(1)
C(11)	7825(5)	5773(3)	2577(2)	29(1)
C(12)	9124(4)	6084(3)	3047(2)	26(1)
C(13)	4675(5)	5480(3)	2218(2)	32(1)
C(14)	4132(5)	6154(4)	1702(2)	41(1)
C(15)	2777(6)	5901(5)	1231(2)	55(1)
C(16)	1944(6)	4967(6)	1288(3)	61(2)
C(17)	2463(6)	4303(5)	1799(3)	55(1)
C(18)	3822(5)	4536(4)	2262(2)	40(1)

Table S5: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***p*-5^{4Br}**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	34(1)	26(1)	42(1)	0(1)	9(1)	3(1)
Br(2)	46(1)	27(1)	48(1)	3(1)	10(1)	6(1)
Br(3)	61(1)	54(1)	54(1)	19(1)	17(1)	18(1)
Br(4)	60(1)	40(1)	63(1)	-3(1)	18(1)	-12(1)
F(1)	30(1)	53(2)	49(2)	2(1)	-4(1)	8(1)
F(2)	40(1)	63(2)	51(2)	-14(1)	-9(1)	-13(1)
F(3)	67(2)	34(1)	59(2)	-18(1)	4(1)	-11(1)
F(4)	30(1)	44(1)	28(1)	-5(1)	12(1)	1(1)
F(5)	19(1)	52(2)	39(1)	-5(1)	10(1)	-1(1)
F(6)	31(1)	60(2)	31(1)	-16(1)	10(1)	-2(1)
F(7)	21(1)	51(2)	35(1)	-7(1)	10(1)	-2(1)
F(8)	56(2)	149(4)	46(2)	7(2)	-6(2)	42(2)
F(9)	37(2)	190(5)	63(2)	-49(3)	-14(2)	-5(2)
F(10)	64(2)	108(3)	88(2)	-43(2)	14(2)	-48(2)
C(1)	24(2)	23(2)	31(2)	-2(2)	10(2)	-1(2)
C(2)	22(2)	33(2)	35(2)	3(2)	8(2)	2(2)
C(3)	27(2)	50(3)	33(2)	-4(2)	2(2)	-9(2)
C(4)	38(2)	31(2)	40(2)	-9(2)	11(2)	-8(2)
C(5)	33(2)	26(2)	32(2)	-1(2)	12(2)	1(2)
C(6)	22(2)	28(2)	24(2)	-1(2)	12(2)	-1(2)
C(7)	22(2)	22(2)	27(2)	-1(2)	4(2)	1(1)
C(8)	27(2)	29(2)	24(2)	1(2)	10(2)	1(2)

C(9)	18(2)	28(2)	36(2)	2(2)	9(2)	2(2)
C(10)	23(2)	28(2)	31(2)	0(2)	6(2)	0(2)
C(11)	28(2)	34(2)	26(2)	-4(2)	9(2)	3(2)
C(12)	19(2)	29(2)	31(2)	0(2)	12(2)	0(2)
C(13)	21(2)	44(2)	31(2)	-7(2)	6(2)	2(2)
C(14)	26(2)	61(3)	37(2)	-2(2)	9(2)	12(2)
C(15)	36(2)	96(4)	33(3)	1(3)	3(2)	20(3)
C(16)	23(2)	121(5)	40(3)	-28(3)	0(2)	1(3)
C(17)	29(2)	79(4)	59(3)	-31(3)	15(2)	-18(2)
C(18)	32(2)	53(3)	37(2)	-10(2)	10(2)	-7(2)

Table S6: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***p*-5^{2Br}-*syn*** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
F(5)	1663(3)	3306(1)	6334(2)	49(1)
F(6)	4073(3)	2384(1)	6313(1)	44(1)
F(7)	8261(3)	4043(1)	6203(1)	45(1)
F(8)	5843(3)	4967(1)	6211(1)	42(1)
C(7)	3658(5)	4165(2)	6279(2)	31(1)
C(8)	5376(5)	4326(2)	6234(2)	32(1)
C(9)	6623(5)	3852(2)	6230(2)	32(1)
C(10)	6244(5)	3186(2)	6256(2)	31(1)
C(11)	4540(6)	3017(2)	6284(2)	33(1)
C(12)	3286(5)	3498(2)	6295(2)	35(1)
C(1A)	1760(7)	5081(3)	5895(3)	34(1)
C(2A)	507(10)	5558(4)	5996(3)	41(2)
C(3A)	-180(8)	5630(4)	6556(4)	44(2)
C(4A)	327(7)	5240(3)	7016(3)	40(1)
C(5A)	1548(8)	4762(3)	6918(3)	36(1)
C(6A)	2307(10)	4664(3)	6361(3)	30(2)
F(1A)	19(5)	5965(2)	5557(2)	62(1)
F(2A)	-1379(5)	6097(2)	6645(2)	60(1)
F(3A)	-329(5)	5329(2)	7566(2)	59(1)
F(4A)	1463(5)	4319(2)	7344(2)	26(1)
Br(1A)	2681(1)	4996(1)	5125(1)	48(1)
C(13A)	7588(11)	2679(4)	6293(3)	32(2)

C(14A)	8467(7)	2596(4)	6823(3)	37(2)
C(15A)	9697(7)	2113(3)	6899(3)	42(1)
C(16A)	10105(7)	1713(3)	6426(3)	42(1)
C(17A)	9266(8)	1781(3)	5889(3)	42(1)
C(18A)	8023(8)	2261(3)	5823(2)	38(1)
F(9A)	8386(6)	3020(3)	7295(2)	42(1)
F(10A)	10520(5)	2039(2)	7421(2)	62(1)
F(11A)	11308(4)	1247(2)	6485(2)	59(1)
F(12A)	9656(5)	1373(2)	5435(2)	60(1)
Br(2A)	6902(1)	2332(1)	5077(1)	50(1)
C(1B)	1390(50)	4781(19)	6653(15)	36(1)
C(2B)	150(40)	5348(17)	6629(19)	40(1)
C(3B)	70(50)	5660(20)	6170(30)	44(2)
C(4B)	940(40)	5573(14)	5651(14)	41(2)
C(5B)	2350(40)	5052(14)	5628(13)	34(1)
C(6B)	2330(60)	4750(20)	6153(17)	30(2)
F(1B)	-790(30)	5447(9)	7094(8)	59(1)
F(2B)	-1140(20)	6182(8)	6084(9)	60(1)
F(3B)	890(20)	5934(9)	5137(10)	67(5)
F(4B)	3280(20)	4995(10)	5193(8)	26(1)
Br(1B)	2043(6)	4394(2)	7400(2)	48(1)
C(13B)	7770(140)	2570(50)	6200(30)	32(2)
C(14B)	7670(90)	2280(30)	5640(30)	38(1)
C(15B)	8920(80)	1800(30)	5650(30)	42(1)
C(16B)	9870(80)	1680(30)	6160(30)	42(1)
C(17B)	10020(70)	2040(30)	6690(20)	42(1)
C(18B)	8820(90)	2540(40)	6700(30)	37(2)
F(9B)	7450(50)	2586(17)	5081(15)	42(1)
F(10B)	9090(50)	1405(17)	5106(18)	60(1)
F(11B)	11150(40)	1193(16)	6060(20)	59(1)
F(12B)	10890(50)	1899(18)	7071(18)	62(1)
Br(2B)	7977(16)	2968(7)	7357(6)	50(1)

Table S7: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***p*-5^{2Br}-*syn***. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(5)	21(1)	34(1)	93(2)	-1(1)	2(1)	-3(1)
F(6)	34(1)	22(1)	77(2)	-2(1)	5(1)	-2(1)
F(7)	23(1)	35(1)	77(2)	4(1)	1(1)	-4(1)
F(8)	35(1)	25(1)	65(2)	4(1)	-3(1)	-5(1)
C(7)	26(2)	26(2)	40(2)	1(2)	-1(2)	3(2)
C(8)	29(2)	21(2)	45(2)	1(2)	-2(2)	-2(2)
C(9)	22(2)	34(2)	42(2)	1(2)	1(2)	-1(2)
C(10)	28(2)	30(2)	34(2)	2(2)	1(2)	2(2)
C(11)	32(2)	24(2)	44(2)	-1(2)	3(2)	1(2)
C(12)	24(2)	33(2)	50(3)	-1(2)	1(2)	0(2)
C(1A)	27(3)	32(3)	43(3)	1(3)	-12(3)	1(3)
C(2A)	36(4)	41(3)	45(5)	6(3)	-7(3)	-1(3)
C(3A)	25(3)	37(3)	70(5)	-7(4)	-3(3)	10(3)
C(4A)	33(3)	33(3)	54(4)	-3(3)	14(3)	2(2)
C(5A)	27(3)	34(3)	47(4)	-2(4)	3(3)	-1(2)
C(6A)	21(2)	24(3)	45(5)	6(3)	-5(4)	-3(2)
F(1A)	59(2)	54(2)	72(3)	15(2)	-15(2)	21(2)
F(2A)	43(2)	44(2)	93(3)	-8(2)	0(2)	18(2)
F(3A)	60(2)	56(2)	61(2)	-9(2)	20(2)	11(2)
F(4A)	16(2)	34(2)	29(2)	1(1)	-4(1)	-3(1)
Br(1A)	45(1)	58(1)	40(1)	5(1)	-2(1)	-1(1)
C(13A)	25(3)	21(4)	52(3)	-2(2)	9(3)	-1(3)
C(14A)	26(4)	30(3)	56(4)	3(3)	2(3)	-1(2)
C(15A)	28(2)	32(2)	65(3)	5(2)	-2(2)	1(2)
C(16A)	28(2)	32(2)	65(3)	5(2)	-2(2)	1(2)
C(17A)	40(4)	28(2)	59(4)	-4(3)	15(3)	3(2)
C(18A)	33(3)	34(2)	47(4)	2(3)	7(3)	2(2)
F(9A)	42(3)	42(2)	41(2)	-2(2)	12(2)	5(2)
F(10A)	57(2)	55(2)	73(2)	5(2)	-22(2)	8(2)
F(11A)	40(2)	37(2)	100(3)	10(2)	4(2)	18(1)
F(12A)	67(2)	45(2)	68(2)	-12(2)	18(2)	15(2)
Br(2A)	57(1)	51(1)	43(1)	-5(1)	2(1)	7(1)
C(1B)	27(3)	34(3)	47(4)	-2(4)	3(3)	-1(2)

C(2B)	33(3)	33(3)	54(4)	-3(3)	14(3)	2(2)
C(3B)	25(3)	37(3)	70(5)	-7(4)	-3(3)	10(3)
C(4B)	36(4)	41(3)	45(5)	6(3)	-7(3)	-1(3)
C(5B)	27(3)	32(3)	43(3)	1(3)	-12(3)	1(3)
C(6B)	21(2)	24(3)	45(5)	6(3)	-5(4)	-3(2)
F(1B)	60(2)	56(2)	61(2)	-9(2)	20(2)	11(2)
F(2B)	43(2)	44(2)	93(3)	-8(2)	0(2)	18(2)
F(3B)	49(10)	62(11)	90(14)	28(10)	-16(10)	8(9)
F(4B)	16(2)	34(2)	29(2)	1(1)	-4(1)	-3(1)
Br(1B)	45(1)	58(1)	40(1)	5(1)	-2(1)	-1(1)
C(13B)	25(3)	21(4)	52(3)	-2(2)	9(3)	-1(3)
C(14B)	33(3)	34(2)	47(4)	2(3)	7(3)	2(2)
C(15B)	40(4)	28(2)	59(4)	-4(3)	15(3)	3(2)
C(16B)	28(2)	32(2)	65(3)	5(2)	-2(2)	1(2)
C(17B)	28(2)	32(2)	65(3)	5(2)	-2(2)	1(2)
C(18B)	26(4)	30(3)	56(4)	3(3)	2(3)	-1(2)
F(9B)	42(3)	42(2)	41(2)	-2(2)	12(2)	5(2)
F(10B)	67(2)	45(2)	68(2)	-12(2)	18(2)	15(2)
F(11B)	40(2)	37(2)	100(3)	10(2)	4(2)	18(1)
F(12B)	57(2)	55(2)	73(2)	5(2)	-22(2)	8(2)
Br(2B)	57(1)	51(1)	43(1)	-5(1)	2(1)	7(1)

Table S8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***p*-5^{2Br}-*anti*** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	1501(1)	5384(1)	1742(1)	36(1)
F(1)	3356(4)	2875(3)	190(2)	46(1)
F(2)	7498(4)	296(3)	500(2)	47(1)
F(3)	10763(4)	-325(3)	2435(2)	49(1)
F(4)	9854(4)	1625(3)	4083(2)	39(1)
F(5)	4863(4)	1393(2)	5566(2)	35(1)
F(6)	3901(4)	2961(2)	7399(2)	34(1)
C(1)	4406(6)	3582(4)	2007(3)	27(1)
C(2)	4912(6)	2594(5)	1170(3)	32(1)
C(3)	7032(6)	1246(4)	1317(3)	33(1)

C(4)	8682(6)	938(4)	2302(3)	33(1)
C(5)	8176(6)	1922(4)	3141(3)	29(1)
C(6)	6030(6)	3242(4)	3036(3)	25(1)
C(7)	5499(6)	4161(4)	4029(3)	26(1)
C(8)	4955(6)	3187(4)	5272(3)	28(1)
C(9)	4449(6)	3992(4)	6216(3)	27(1)

Table S9: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***p*-5^{2Br}-*anti***. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	33(1)	38(1)	36(1)	-14(1)	-1(1)	0(1)
F(1)	52(1)	60(1)	33(1)	-27(1)	-8(1)	-9(1)
F(2)	62(1)	48(1)	42(1)	-33(1)	13(1)	-10(1)
F(3)	50(1)	42(1)	54(1)	-24(1)	2(1)	12(1)
F(4)	44(1)	37(1)	31(1)	-9(1)	-9(1)	5(1)
F(5)	58(1)	22(1)	28(1)	-10(1)	6(1)	-11(1)
F(6)	52(1)	28(1)	20(1)	-7(1)	8(1)	-9(1)
C(1)	31(2)	27(2)	24(1)	-9(1)	3(1)	-6(1)
C(2)	36(2)	39(2)	25(2)	-16(1)	1(1)	-10(1)
C(3)	46(2)	33(2)	28(2)	-18(1)	10(1)	-12(2)
C(4)	36(2)	26(2)	35(2)	-13(1)	8(1)	0(1)
C(5)	36(2)	28(2)	23(1)	-9(1)	1(1)	-5(1)
C(6)	33(2)	21(1)	22(1)	-9(1)	6(1)	-7(1)
C(7)	31(2)	27(2)	22(1)	-11(1)	1(1)	-2(1)
C(8)	37(2)	24(1)	27(2)	-11(1)	1(1)	-4(1)
C(9)	35(2)	24(1)	20(1)	-5(1)	2(1)	-4(1)

Table S10: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***m*-5^{4Br} TDAI** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
I(2)	1427(1)	2500	5000	50(1)
N(1)	2738(4)	7500	5000	73(2)
N(2)	1173(2)	6735(6)	4596(1)	53(1)
C(19)	3104(4)	6875(11)	4729(2)	99(3)
C(20)	2080(4)	7500	5000	58(2)
C(21)	1496(3)	7193(7)	4853(2)	49(1)
C(22)	466(3)	6423(10)	4613(2)	65(2)
C(23)	1511(4)	6065(9)	4328(2)	69(2)
F(4)	2675(2)	97(4)	3832(1)	54(1)
F(5)	3270(2)	5964(4)	3916(1)	68(1)
F(6)	2136(2)	6907(4)	3640(1)	70(1)
F(7)	1265(2)	4473(4)	3465(1)	63(1)
C(7)	3000(3)	2997(7)	3877(1)	46(1)
C(8)	2851(3)	4730(7)	3829(2)	54(2)
C(9)	2271(3)	5212(7)	3687(2)	55(2)
C(10)	1827(3)	3964(7)	3597(1)	48(1)
C(11)	1948(3)	2209(6)	3646(1)	43(1)
C(12)	2539(3)	1802(7)	3784(1)	45(1)
Br(1A)	4069(2)	2897(3)	3364(1)	74(1)
Br(2A)	2881(3)	1927(10)	4562(2)	51(1)
Br(3A)	2080(3)	1177(10)	2964(2)	56(1)
Br(4A)	1072(4)	890(10)	4166(2)	41(1)
F(1A)	5308(5)	2010(20)	3731(3)	114(4)
F(2A)	5422(6)	1030(30)	4332(3)	105(4)
F(3A)	4372(9)	1010(30)	4705(3)	85(3)
F(8A)	147(2)	-1710(5)	3883(1)	76(1)
F(9A)	100(20)	-2800(40)	3256(8)	73(6)
F(10A)	827(16)	-1320(40)	2853(3)	77(7)
C(1A)	4169(10)	2480(30)	3795(3)	56(4)
C(2A)	4761(5)	1950(18)	3910(3)	64(2)
C(3A)	4841(6)	1550(20)	4226(4)	60(3)
C(4A)	4303(7)	1510(20)	4414(3)	64(2)
C(5A)	3719(10)	1940(30)	4299(6)	45(3)

C(6A)	3636(3)	2471(8)	4017(2)	59(2)
C(13A)	1462(3)	874(6)	3551(1)	45(1)
C(14A)	1037(3)	172(7)	3769(1)	47(1)
C(15A)	579(3)	-1032(8)	3676(2)	58(1)
C(16A)	529(3)	-1527(8)	3370(2)	62(2)
C(17A)	956(3)	-849(7)	3152(2)	58(1)
C(18A)	1455(7)	270(20)	3238(7)	47(1)
Br(1B)	4299(4)	3118(7)	3488(2)	104(2)
Br(2B)	2962(6)	1836(19)	4610(3)	64(2)
Br(3B)	1970(8)	1125(14)	2917(3)	73(2)
Br(4B)	1135(5)	706(14)	4231(3)	39(1)
F(1B)	5401(8)	1980(40)	3908(5)	114(4)
F(2B)	5382(11)	1040(50)	4494(5)	105(4)
F(3B)	4225(17)	800(60)	4802(6)	85(3)
F(8B)	147(2)	-1710(5)	3883(1)	76(1)
F(9B)	60(30)	-2530(60)	3323(12)	78(9)
F(10B)	980(20)	-1500(50)	2861(4)	72(8)
C(1B)	4269(18)	2410(60)	3915(6)	56(4)
C(2B)	4836(10)	1940(40)	4072(7)	64(2)
C(3B)	4788(11)	1370(40)	4371(5)	60(3)
C(4B)	4185(12)	1340(40)	4508(6)	64(2)
C(5B)	3574(19)	1910(60)	4371(11)	45(3)
C(6B)	3636(3)	2471(8)	4017(2)	59(2)
C(13B)	1462(3)	874(6)	3551(1)	45(1)
C(14B)	1037(3)	172(7)	3769(1)	47(1)
C(15B)	579(3)	-1032(8)	3676(2)	58(1)
C(16B)	529(3)	-1527(8)	3370(2)	62(2)
C(17B)	956(3)	-849(7)	3152(2)	58(1)
C(18B)	1381(10)	420(30)	3244(9)	47(1)
N(3A)	2350(7)	6791(14)	2500	74(4)
N(5A)	3803(4)	8356(11)	2921(2)	61(2)
C(24A)	3496(3)	7978(8)	2660(1)	56(2)
C(25A)	2951(7)	7489(16)	2500	56(3)
C(26A)	2090(6)	6083(15)	2795(3)	87(4)
C(27A)	3479(16)	8000(40)	3197(5)	72(4)
C(28A)	4490(6)	8920(20)	2915(3)	85(4)
I(1A)	3453(3)	2862(5)	2500	62(1)
N(3B)	4636(8)	9190(30)	2500	49(5)
N(5B)	3200(8)	7470(20)	2929(4)	66(5)

C(24B)	3496(3)	7978(8)	2660(1)	56(2)
C(25B)	4043(16)	8420(30)	2500	63(8)
C(26B)	4890(10)	9890(30)	2789(4)	61(5)
C(27B)	3570(30)	7770(90)	3267(12)	72(4)
C(28B)	2573(12)	6560(30)	2935(6)	82(7)
I(1B)	3633(4)	3072(10)	2500	62(1)

Table S11: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***m*-5^{4Br} TDAI**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(2)	52(1)	45(1)	51(1)	4(1)	0	0
N(1)	36(4)	66(5)	116(7)	-24(5)	0	0
N(2)	50(3)	52(3)	58(3)	-2(2)	2(2)	6(2)
C(19)	48(4)	73(5)	176(9)	-30(6)	24(5)	10(4)
C(20)	49(5)	40(4)	84(6)	-9(4)	0	0
C(21)	42(3)	31(3)	74(4)	-2(2)	-1(3)	2(2)
C(22)	56(4)	76(4)	62(4)	7(3)	-18(3)	-3(3)
C(23)	92(5)	55(4)	61(4)	-5(3)	12(4)	10(4)
F(4)	61(2)	28(1)	72(2)	-2(1)	9(2)	1(1)
F(5)	59(2)	39(2)	104(3)	-10(2)	17(2)	-17(2)
F(6)	76(2)	25(2)	109(3)	1(2)	16(2)	-2(2)
F(7)	67(2)	39(2)	82(2)	5(2)	3(2)	1(2)
C(7)	45(3)	36(3)	57(3)	-5(2)	23(2)	-4(2)
C(8)	56(3)	36(3)	69(4)	-8(3)	24(3)	-11(3)
C(9)	64(4)	25(3)	78(4)	-2(3)	22(3)	-5(2)
C(10)	52(3)	37(3)	55(3)	1(2)	13(3)	1(2)
C(11)	55(3)	31(3)	42(3)	-3(2)	20(2)	-5(2)
C(12)	51(3)	31(3)	54(3)	-3(2)	19(3)	-2(2)
Br(1A)	67(1)	79(1)	77(1)	11(1)	35(1)	7(1)
Br(2A)	48(1)	61(1)	45(2)	-2(1)	-7(2)	2(1)
Br(3A)	66(2)	58(1)	44(2)	-7(1)	6(1)	-5(1)
Br(4A)	46(1)	48(1)	30(2)	17(1)	2(1)	2(1)
F(1A)	52(4)	163(6)	126(10)	50(10)	42(6)	30(4)
F(2A)	53(3)	119(4)	143(12)	-6(12)	-14(8)	25(3)
F(3A)	72(9)	93(7)	90(10)	7(8)	-15(7)	9(6)

F(8A)	69(2)	76(2)	82(2)	16(2)	6(2)	-33(2)
F(9A)	91(14)	48(9)	81(13)	-20(8)	-17(10)	-30(9)
F(10A)	108(18)	68(7)	55(6)	-14(5)	-7(6)	26(8)
C(1A)	43(7)	64(4)	60(11)	13(10)	11(8)	5(5)
C(2A)	44(4)	75(4)	74(7)	0(5)	13(4)	8(3)
C(3A)	43(5)	64(6)	74(12)	26(9)	13(7)	5(4)
C(4A)	44(4)	75(4)	74(7)	0(5)	13(4)	8(3)
C(5A)	23(10)	43(3)	70(14)	-13(7)	21(6)	0(7)
C(6A)	43(3)	44(3)	89(5)	-9(3)	19(3)	-3(2)
C(13A)	55(3)	27(2)	52(3)	2(2)	4(2)	2(2)
C(14A)	57(3)	33(2)	52(2)	1(2)	2(2)	4(2)
C(15A)	68(3)	45(2)	62(3)	2(2)	-2(2)	-4(2)
C(16A)	68(4)	35(3)	84(5)	-5(3)	-14(4)	-14(3)
C(17A)	68(3)	45(2)	62(3)	2(2)	-2(2)	-4(2)
C(18A)	57(3)	33(2)	52(2)	1(2)	2(2)	4(2)
Br(1B)	82(3)	130(3)	101(3)	-5(2)	55(3)	-2(2)
Br(2B)	71(4)	72(2)	49(3)	-3(2)	-16(2)	14(2)
Br(3B)	134(6)	51(2)	33(2)	3(1)	13(3)	1(3)
Br(4B)	45(2)	44(2)	29(3)	17(2)	-2(2)	-2(1)
F(1B)	52(4)	163(6)	126(10)	50(10)	42(6)	30(4)
F(2B)	53(3)	119(4)	143(12)	-6(12)	-14(8)	25(3)
F(3B)	72(9)	93(7)	90(10)	7(8)	-15(7)	9(6)
F(8B)	69(2)	76(2)	82(2)	16(2)	6(2)	-33(2)
F(9B)	84(11)	62(15)	88(19)	-36(9)	-4(13)	-9(11)
F(10B)	74(13)	65(14)	78(11)	-34(8)	-21(7)	-9(13)
C(1B)	43(7)	64(4)	60(11)	13(10)	11(8)	5(5)
C(2B)	44(4)	75(4)	74(7)	0(5)	13(4)	8(3)
C(3B)	43(5)	64(6)	74(12)	26(9)	13(7)	5(4)
C(4B)	44(4)	75(4)	74(7)	0(5)	13(4)	8(3)
C(5B)	23(10)	43(3)	70(14)	-13(7)	21(6)	0(7)
C(6B)	43(3)	44(3)	89(5)	-9(3)	19(3)	-3(2)
C(13B)	55(3)	27(2)	52(3)	2(2)	4(2)	2(2)
C(14B)	57(3)	33(2)	52(2)	1(2)	2(2)	4(2)
C(15B)	68(3)	45(2)	62(3)	2(2)	-2(2)	-4(2)
C(16B)	68(4)	35(3)	84(5)	-5(3)	-14(4)	-14(3)
C(17B)	68(3)	45(2)	62(3)	2(2)	-2(2)	-4(2)
C(18B)	57(3)	33(2)	52(2)	1(2)	2(2)	4(2)
N(3A)	80(9)	27(5)	114(11)	0	0	1(6)
N(5A)	76(6)	61(5)	47(4)	8(4)	-5(4)	4(4)

C(24A)	59(4)	53(3)	56(3)	5(3)	4(3)	1(3)
C(25A)	72(9)	37(6)	58(8)	0	0	1(6)
C(26A)	69(8)	53(6)	137(12)	2(7)	29(8)	-9(6)
C(27A)	92(12)	92(11)	32(12)	18(8)	-13(8)	-2(8)
C(28A)	72(8)	113(10)	68(7)	1(7)	-15(6)	27(8)
I(1A)	53(2)	54(1)	79(1)	0	0	12(1)
N(3B)	21(8)	75(13)	50(10)	0	0	-13(8)
N(5B)	74(11)	52(9)	71(11)	-7(7)	16(9)	-17(8)
C(24B)	59(4)	53(3)	56(3)	5(3)	4(3)	1(3)
C(25B)	100(20)	44(13)	47(13)	0	0	29(14)
C(26B)	59(11)	65(11)	61(11)	2(9)	2(9)	14(9)
C(27B)	92(12)	92(11)	32(12)	18(8)	-13(8)	-2(8)
C(28B)	74(15)	82(15)	89(16)	-1(12)	41(13)	1(12)
I(1B)	53(2)	54(1)	79(1)	0	0	12(1)

Table S12: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ***m*-5^{4Br} TDAI**.

	x	y	z	U(eq)
H(19A)	3286	7871	4615	149
H(19B)	2809	6219	4592	149
H(19C)	3462	6117	4798	149
H(22A)	265	6688	4412	97
H(22B)	274	7173	4774	97
H(22C)	385	5201	4666	97
H(23A)	1225	6149	4145	104
H(23B)	1627	4843	4364	104
H(23C)	1910	6745	4293	104
H(26A)	1645	5642	2761	130
H(26B)	2081	7005	2952	130
H(26C)	2372	5131	2866	130
H(27A)	3754	8344	3373	87
H(27B)	3387	6746	3209	87
H(27C)	3065	8646	3203	87
H(28A)	4653	9032	3128	127
H(28B)	4522	10048	2809	127

H(28C)	4754	8057	2803	127
H(26D)	5369	9985	2776	92
H(26E)	4772	9116	2962	92
H(26F)	4702	11048	2826	92
H(27D)	3246	8121	3424	108
H(27E)	3902	8688	3245	108
H(27F)	3782	6687	3332	108
H(28D)	2643	5340	2996	122
H(28E)	2374	6593	2727	122
H(28F)	2280	7119	3085	122

Table S13: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ 10^3) for ***p*-5^{4Br} TDAI** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
I(1A^a)	5000	1657(1)	2500	50(1)
I(1B^b)	4690(30)	1681(15)	3000(60)	50(1)
N(1)	5000	690(3)	7500	48(1)
N(2)	4174(2)	2235(2)	6578(5)	40(1)
C(10)	4459(2)	335(2)	6709(7)	50(1)
C(11)	5000	1335(3)	7500	40(1)
C(12)	4700(2)	1919(2)	7131(5)	34(1)
C(13)	4203(2)	2935(2)	6148(6)	47(1)
C(14)	3651(2)	1854(2)	5747(7)	48(1)
Br(1A^a)	4161(1)	6701(2)	6054(4)	57(1)
Br(2A^a)	1661(1)	5869(1)	4138(2)	55(1)
F(1A^a)	2310(4)	4543(3)	4341(10)	93(2)
F(2A^a)	3521(5)	4258(3)	5179(11)	116(3)
F(3A^a)	4361(3)	5223(5)	5974(11)	99(3)
C(1A^a)	3579(4)	6034(6)	5480(15)	38(2)
C(2A^a)	3760(6)	5406(10)	5523(19)	76(4)
C(3A^a)	3335(7)	4889(5)	5121(14)	66(3)
C(4A^a)	2713(6)	5037(5)	4707(13)	59(2)
C(5A^a)	2507(4)	5685(4)	4679(12)	40(2)
C(6A^a)	2939(3)	6195(6)	5059(14)	29(2)
Br(1B^b)	4237(2)	6904(2)	6097(8)	37(1)
Br(2B^b)	1893(3)	5625(3)	4244(5)	89(1)

F(1B^b)	2729(9)	4446(7)	4510(20)	93(2)
F(2B^b)	3998(10)	4395(7)	5280(30)	116(3)
F(3B^b)	4667(7)	5489(10)	5970(30)	99(3)
C(1B^b)	3759(11)	6173(15)	5610(40)	38(2)
C(2B^b)	4022(14)	5450(20)	5640(50)	76(4)
C(3B^b)	3699(12)	4974(13)	5300(30)	66(3)
C(4B^b)	3054(16)	4994(13)	4900(30)	59(2)
C(5B^b)	2760(8)	5584(11)	4810(30)	40(2)
C(6B^b)	3131(10)	6144(15)	5210(40)	29(2)
F(4)	2848(1)	6934(1)	8160(3)	41(1)
F(5)	2381(1)	8160(1)	8066(3)	41(1)
C(7)	2745(2)	6859(2)	5043(5)	32(1)
C(8)	2680(2)	7205(2)	6594(5)	32(1)
C(9)	2442(2)	7840(2)	6544(5)	34(1)

Table S14: Anisotropic displacement parameters ($Å^2$ x 10^3) for ***p*-5^{4Br} TDAI**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1A^a)	56(1)	50(1)	44(1)	0	16(1)	0
I(1B^b)	56(1)	50(1)	44(1)	0	16(1)	0
N(1)	37(2)	37(3)	66(4)	0	-18(2)	0
N(2)	35(2)	42(2)	43(2)	-1(2)	-9(1)	8(2)
C(10)	41(2)	43(2)	65(3)	-5(2)	-11(2)	-2(2)
C(11)	38(3)	42(3)	39(3)	0	-8(2)	0
C(12)	34(2)	37(2)	31(2)	0(2)	-4(2)	1(2)
C(13)	49(2)	44(2)	48(3)	8(2)	-2(2)	11(2)
C(14)	27(2)	59(3)	56(3)	-6(2)	-7(2)	9(2)
Br(1A^a)	29(1)	95(2)	46(1)	-3(1)	-6(1)	-6(1)
Br(2A^a)	46(1)	60(1)	58(1)	-1(1)	-5(1)	-24(1)
F(1A^a)	141(6)	38(2)	97(3)	-3(2)	-12(5)	-21(4)
F(2A^a)	186(8)	45(3)	115(4)	-4(3)	-16(7)	56(5)
F(3A^a)	78(5)	123(8)	94(3)	-10(4)	-16(5)	67(5)
C(1A^a)	36(7)	44(6)	30(3)	-5(4)	-13(4)	3(4)
C(2A^a)	86(10)	90(6)	50(4)	1(4)	-5(7)	69(11)
C(3A^a)	97(9)	39(4)	59(5)	-2(3)	-12(7)	30(7)
C(4A^a)	91(7)	34(3)	50(4)	0(3)	-17(5)	6(5)
C(5A^a)	49(6)	32(4)	38(3)	0(3)	-5(4)	3(4)
C(6A^a)	24(5)	35(3)	25(3)	2(2)	-9(4)	5(5)
Br(1B^b)	23(1)	48(1)	37(1)	-3(1)	-4(1)	-2(1)
Br(2B^b)	78(2)	101(3)	88(2)	-18(2)	0(2)	-58(2)
F(1B^b)	141(6)	38(2)	97(3)	-3(2)	-12(5)	-21(4)
F(2B^b)	186(8)	45(3)	115(4)	-4(3)	-16(7)	56(5)
F(3B^b)	78(5)	123(8)	94(3)	-10(4)	-16(5)	67(5)
C(1B^b)	36(7)	44(6)	30(3)	-5(4)	-13(4)	3(4)
C(2B^b)	86(10)	90(6)	50(4)	1(4)	-5(7)	69(11)
C(3B^b)	97(9)	39(4)	59(5)	-2(3)	-12(7)	30(7)
C(4B^b)	91(7)	34(3)	50(4)	0(3)	-17(5)	6(5)
C(5B^b)	49(6)	32(4)	38(3)	0(3)	-5(4)	3(4)
C(6B^b)	24(5)	35(3)	25(3)	2(2)	-9(4)	5(5)
F(4)	47(1)	48(1)	27(1)	4(1)	-4(1)	-1(1)
F(5)	46(1)	48(1)	27(1)	-9(1)	-2(1)	-2(1)

C(7)	28(2)	39(2)	30(2)	-1(2)	-4(1)	-9(2)
C(8)	27(2)	42(2)	26(2)	1(2)	-3(1)	-7(2)
C(9)	29(2)	46(2)	26(2)	-7(2)	-2(1)	-10(2)

Table S15: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ***p*-5^{4Br} TDAI**.

	x	y	z	U(eq)
H(10A)	4351	501	5510	76
H(10B)	4102	397	7433	76
H(10C)	4559	-134	6652	76
H(13A)	4357	2989	4968	71
H(13B)	4489	3157	7027	71
H(13C)	3784	3128	6160	71
H(14A)	3751	1717	4559	72
H(14B)	3271	2125	5657	72
H(14C)	3581	1466	6468	72

B.3.) Additional non-covalent interactions found in the crystal data

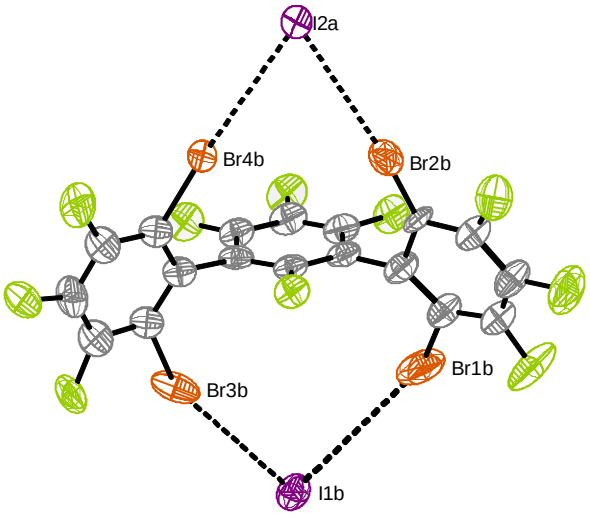


Figure S1: Less probable interaction which can be found due to a disorder of one of the iodides (I1b instead of I1a) in the crystal of ***m*-5^{4Br} TDAI**.

B.4.) Summary of halogen bonding contacts

Table S16: Halogen bonding angles and distances including their standard deviations (below 100% van der Waals radius and above C-Br--X angles of 150°).

Compound	Interaction	d_{Br-X} [A]	$\sphericalangle_{CBrX}$ [°]	%V.D.W. radius
2183888 (***m*-5^{4Br}**)	C1-Br1···Br2	3.4101(7)	153.773(127)	92.2
	C5-Br2···Br1	3.6095(7)	165.545(128)	97.6
2183889 (***m*-5^{4Br} TDAI**)	C5A-Br2A···I2	3.5388(67)	172.508(669)	91.7
	C5B-Br2B···I2	3.5859(124)	164.821(1581)	92.9
	C14AB-Br4A···I2	3.8571(85)	171.381(434)	99.9
	C14AB-Br4B···I2	3.6271(125)	168.466(572)	94.0
	C1A-Br1A···I1B	3.8161(39)	169.451(424)	98.9
	C18A-Br3A···I1A	3.6723(84)	173.136(604)	95.1
	C18A-Br3A···I1A	3.7590(158)	161.619(951)	97.4
2183890 (***p*-5^{4Br}**)	C1-Br1···Br3	3.4929(7)	155.782(119)	94.4
2183893 (***p*-5^{4Br} TDAI**)	C1A-Br1A···I1B1	3.7531(363)	154.805(645)	97.2
	C1B-Br1B···I1A	3.4844(39)	171.702(904)	90.3
	C1B-Br1B···I1B2	3.7174(460)	175.773(1042)	96.3
	C5A-Br2A···I1B1/2	3.6069(542)	157.391(880)	93.4

C.) NMR-Spectra

C.1.) 2,2",6,6"-Tetrabromo-decafluoro-1,3-terphenyl

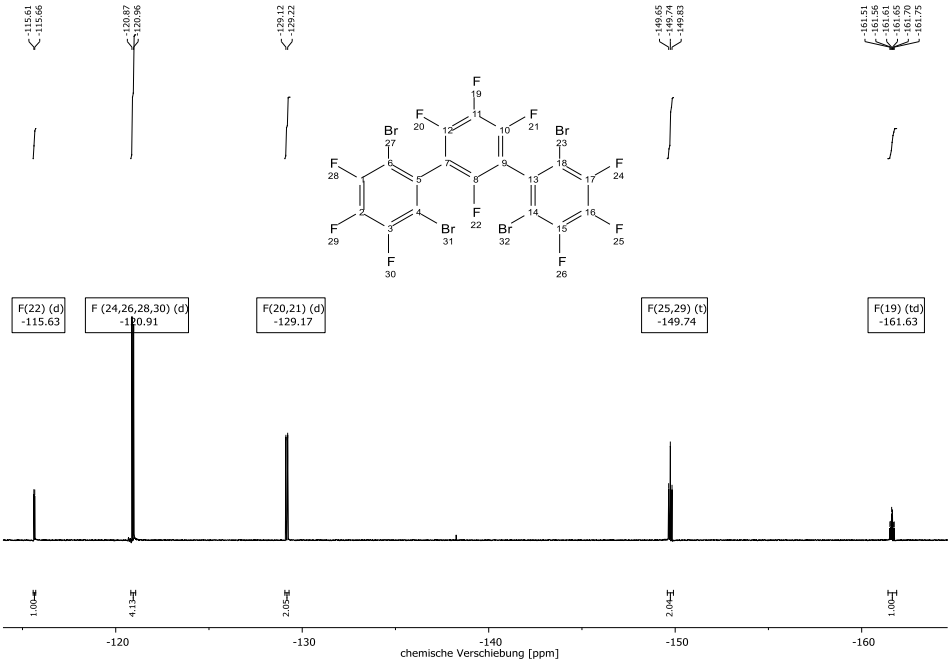


Figure S2: ^{19}F-NMR of 2,2",6,6"-Tetrabromo-decafluoro-1,3-terphenyl.

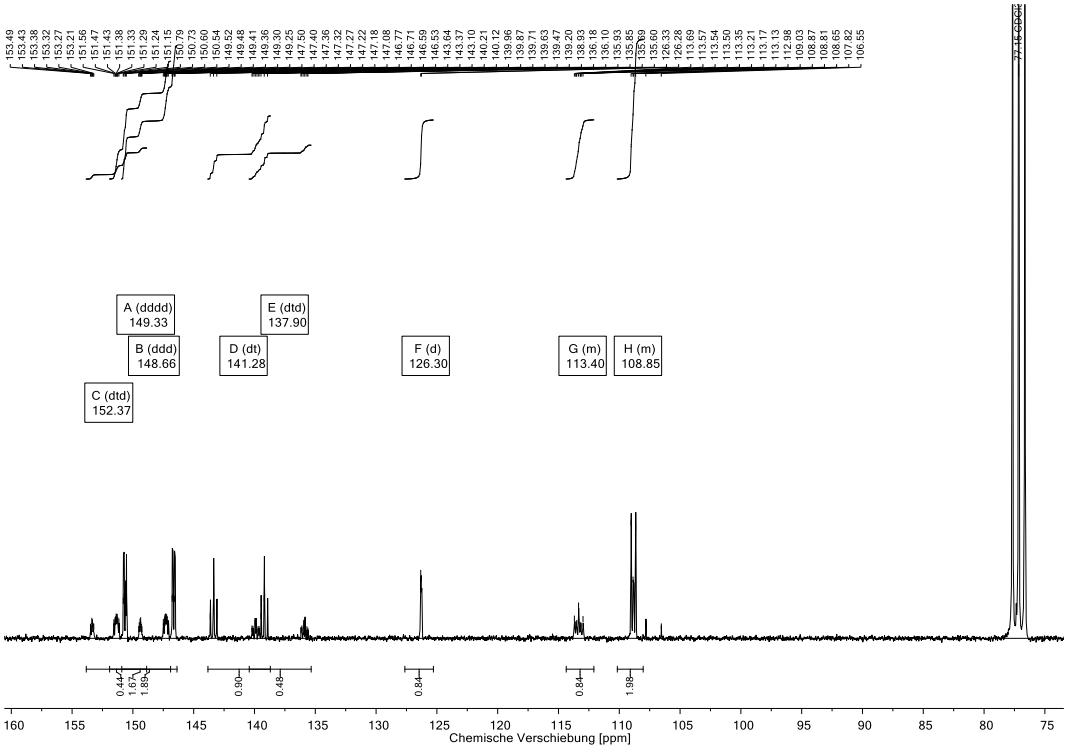


Figure S3: ^{13}C-NMR of 2,2",6,6"-Tetrabromo-decafluoro-1,3-terphenyl.

C.2.) 2,2",6,6"-Tetrabromo-decafluoro-1,4-terphenyl

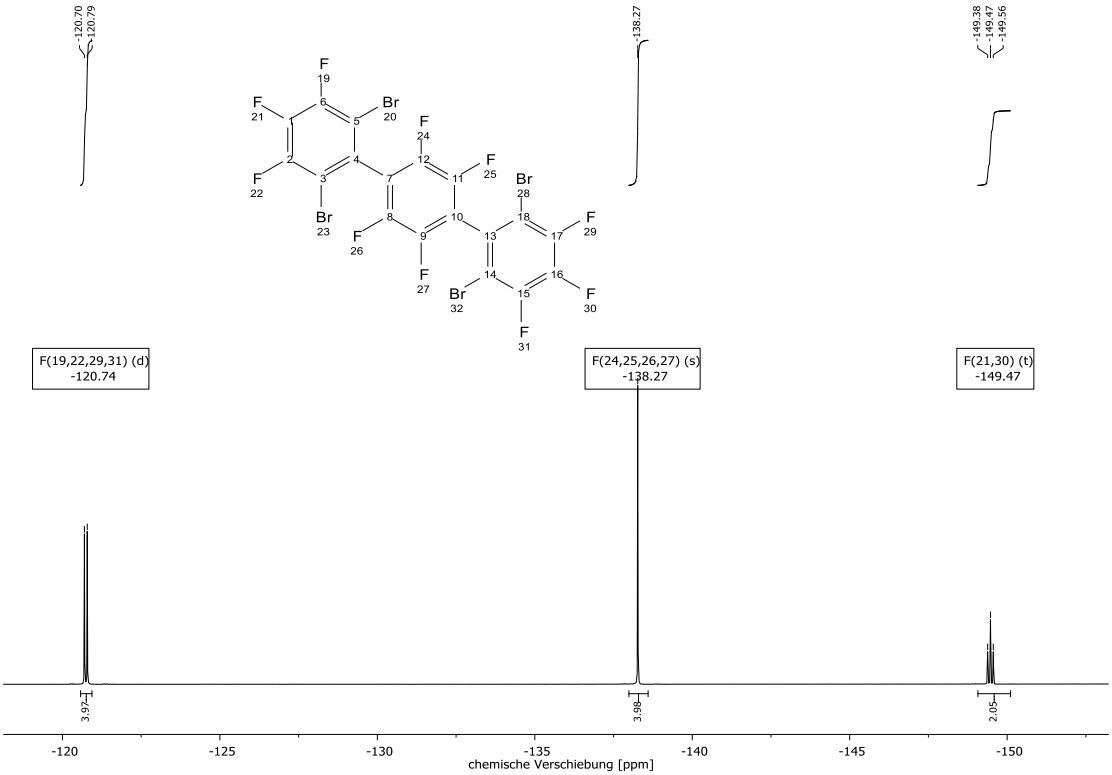


Figure S4: ^{19}F-NMR of 2,2",6,6"-Tetrabromo-decafluoro-1,4-terphenyl.

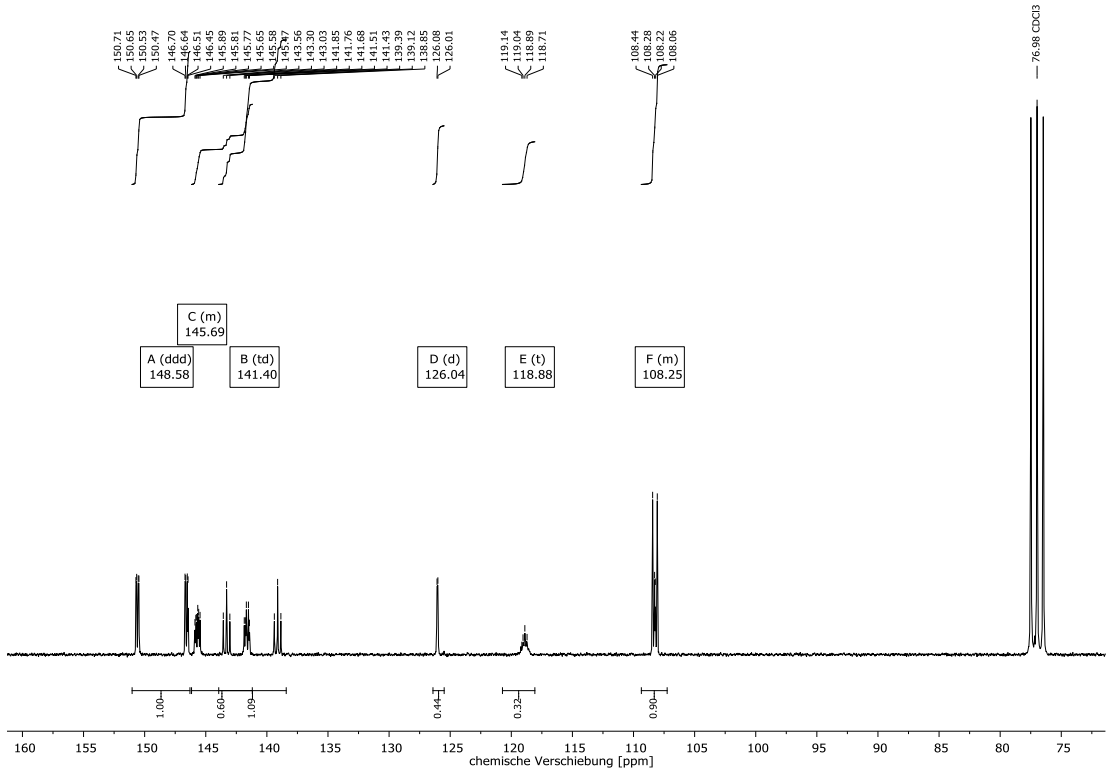


Figure S5: ^{13}C-NMR of 2,2",6,6"-Tetrabromo-decafluoro-1,4-terphenyl.

C.3.) *syn*-2,2''-Dibromo-dodecafluoro-1,4-terphenyl
anti-2,2''-Dibromo-dodecafluoro-1,4-terphenyl

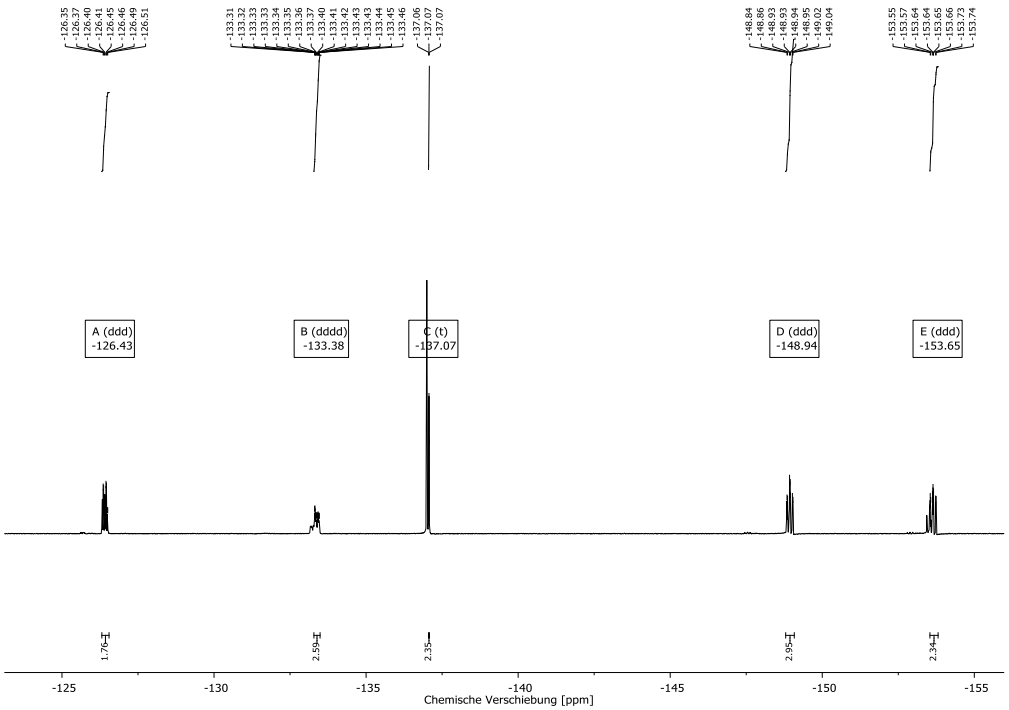


Figure S6: ^{19}F-NMR presumable of *syn*-2,2''-Dibromo-dodecafluoro-1,4-terphenyl.

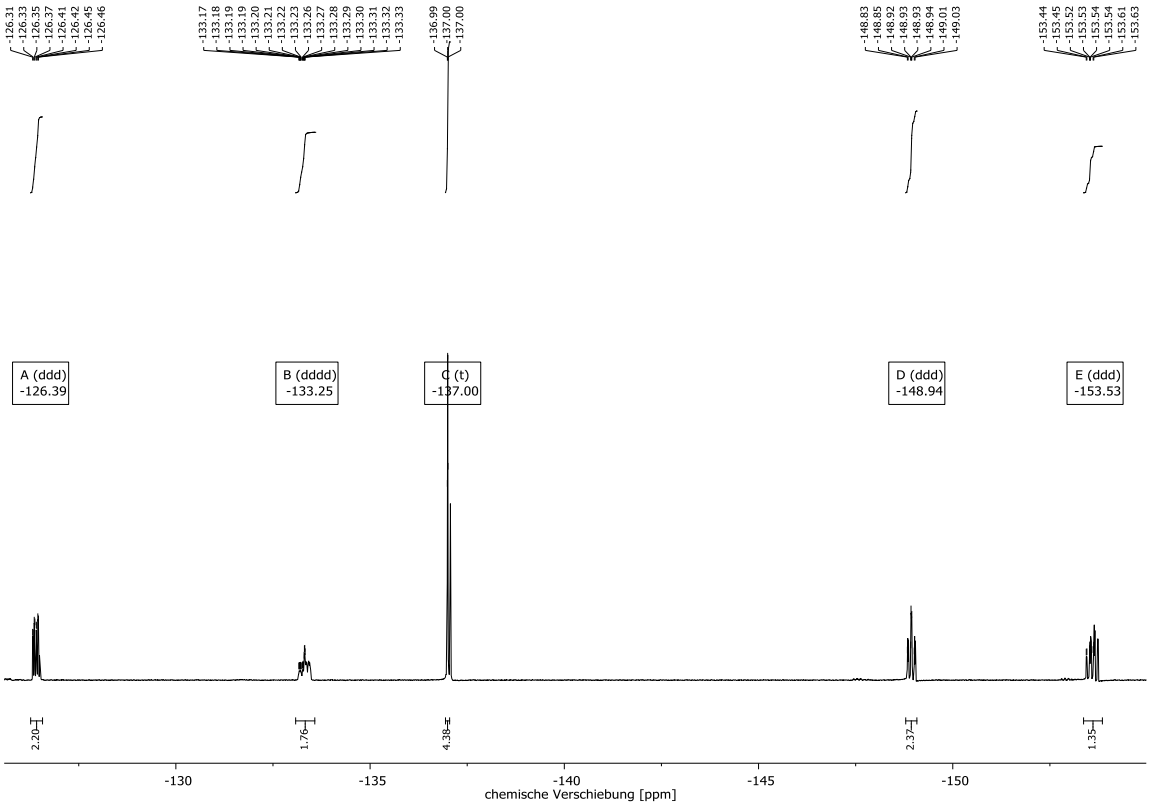


Figure S7: ^{19}F-NMR presumable of *anti*-2,2''-Dibromo-dodecafluoro-1,4-terphenyl.

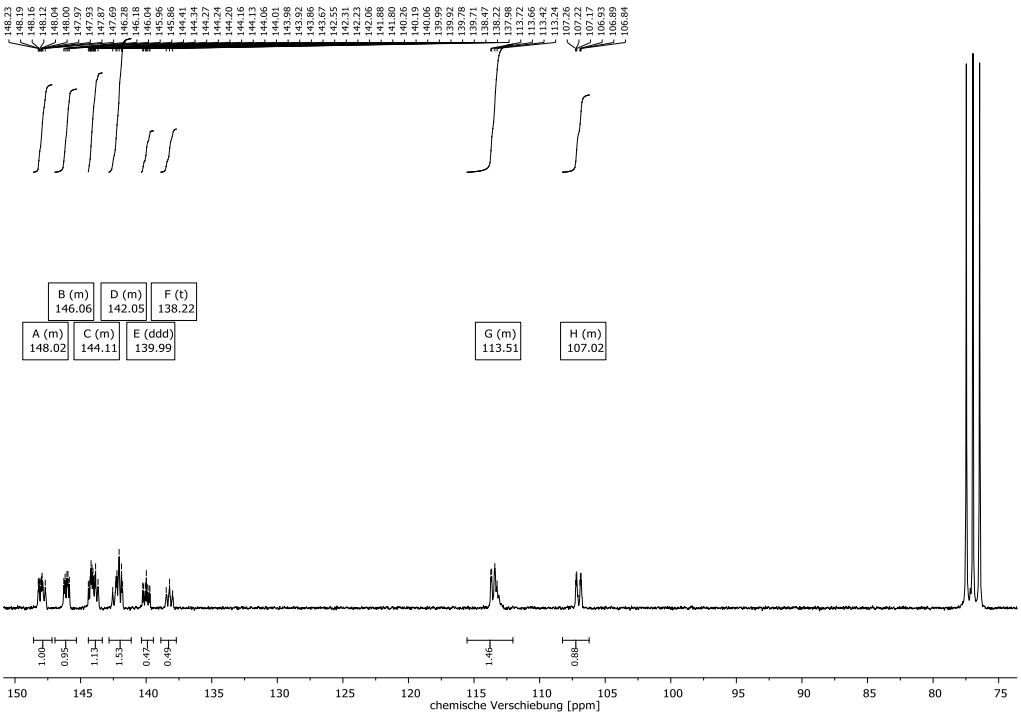


Figure S8: ^{13}C-NMR of the mixture *syn*-/*anti*-2,2''-Dibromo-dodecafluoro-1,4-terphenyl.

C.4.) 1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene

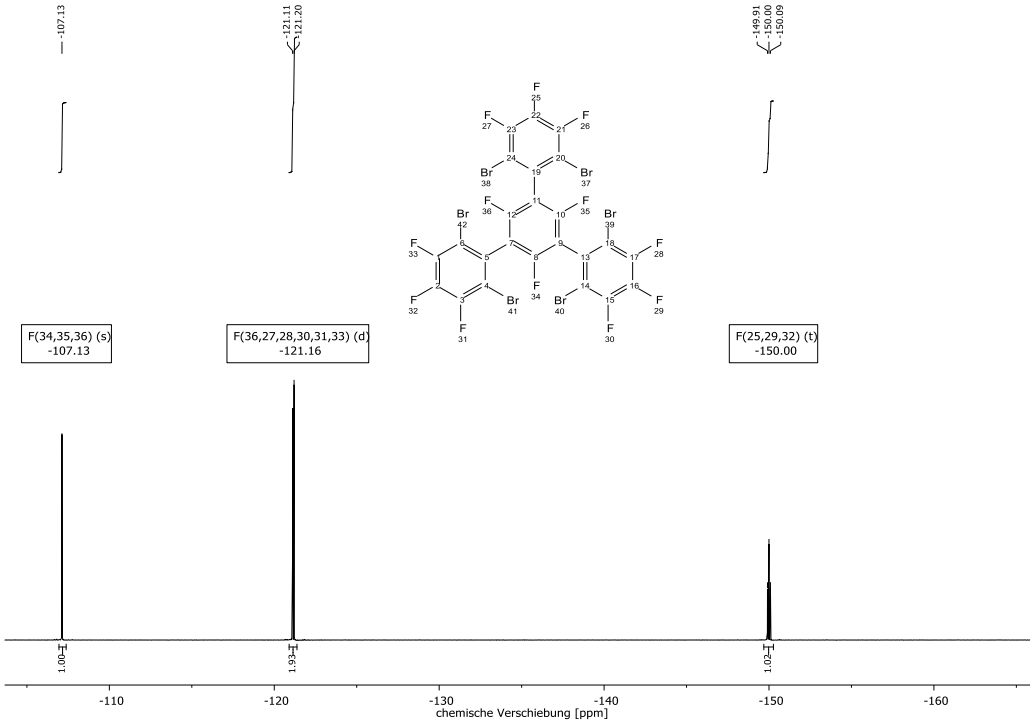


Figure S9: ^{19}F-NMR 1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene.

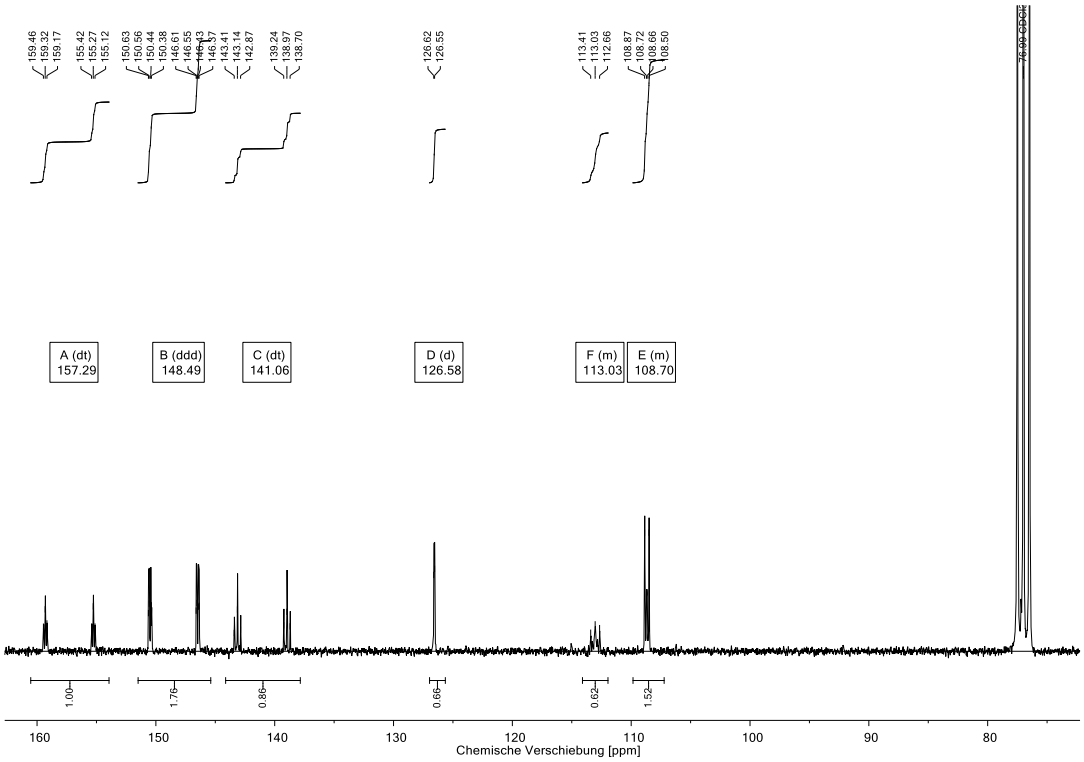


Figure S10: ^{13}C-NMR 1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene.

D. 1) NMR-Titrations

D 1.1) General information

Chemicals

All deuterated solvents were purchased from Deutero GmbH, dried and stored over molecular sieve.

General Procedure

For pipetting Hamilton® syringes were used. All experiments were conducted at room temperature and in Norell® 502 NMR-Tubes. The following concentrations were used for the corresponding Host and Guest solutions:

Table S17: Concentrations of the stock solutions of the different compounds used for titrations

compound	concentration [mM/L]
2,2",6,6"-Tetrabromo-decafluoro-1,3-terphenyl ***m-5^{4Br}***	60.6
2,2",6,6"-Tetrabromo-decafluoro-1,4-terphenyl ***p-5^{4Br}***	60.6
1,3,5-Tris-(2,6-dibromo-3,4,5-trifluorophenyl)-2,4,6-trifluorobenzene ***m-5^{6Br}***	30.3
guest solutions for titrations with ***m-5^{4Br}*** and ***p-5^{4Br}*** (TBA-Cl, TOA-Br)	501.6
guest solutions for titrations with ***m-5^{6Br}*** (TBA-Cl, TOA-Br and orthoamide)	250.8

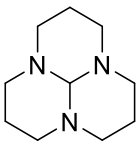
As internal standard a solution of 1 µl of 1,3,5-trifluorobenzene in 1 ml of solvent was used. The NMR tube was filled with 100 µl of the host solution, 100 µl of the reference solution and filled to a total volume of 600 µl with solvent. For each measured point, a certain amount of Guest solution was added. The NMR-spectra were measured with a *Bruker* DPX-250. Each ^{19}F-NMR-spectra was measured with 32 scans. To determine the binding constants the displacements of the fluorine atoms in the ortho, para and meta positions to the bromine atom were observed relative to the signal of the standard. The measured shifts (Δ ppm) were plotted against the guest equivalents and the resulting curve was analyzed. For the analysis, the website supramolecular.org[5] was used.

D 1.2.) Titrations results

Table S18: Binding constants and Gibbs free energies obtained from titrations of the bromine-based donors with different guests and binding constants of the iodinated analogues from previous works.[6] Due to the weak interaction of the bromine-based donors, a second binding event could not be detected, thus the second binding events of the iodinated donors are also not listed here. All Titrations were performed at 298.15 K.

Donor	Guest	Solvent	K [M-1]	ΔG [kcal/mol]
m-5^{4Br}	TBA-Cl	THF	26.8 ± 0.5	-1.95 ± 0.01
	TOA-Br		10.7 ± 1.3	-1.40 ± 0.07
	TOA-I		decomposition	
m-1^{4I}	TBA-Cl	THF	$1.5x10^4$ ± $3.0x10^3$	-5.80 ± 0.11
	TBA-Br		$1.1x10^4$ ± $3.4x10^3$	-5.60 ± 0.19
	TOA-I		$5.6x10^3$ ± $1.2x10^3$	-5.20 ± 0.12
p-5^{4Br}	TBA-Cl	THF	15.4 ± 1.5	-1.62 ± 0.06
	TOA-Br		17.4 ± 1.7	-1.70 ± 0.06
	TOA-I		decomposition	
p-1^{4I}	TBA-Cl	THF	$6.3x10^4$ ± $5.3x10^3$	-6.65 ± 0.05
	TBA-Br		$7.3x10^4$ ± $6.2x10^3$	-6.76 ± 0.05
	TOA-I		$1.7x10^4$ ± $9.3x10^2$	-5.86 ± 0.03
m-5^{6Br}	TBA-Cl	THF	128 ± 18.4	-2.9 ± 0.09
	TOA-Br		290.5 ± 50.1	-3.38 ± 0.16
	TOA-I		decomposition	
	Orthoamide	Cyclo-hexane	24.4 ± 1.3	-1.9 ± 0.03
m-1^{6I}	TBA-Cl	THF	$5.0x10^5$ ± $4.0x10^5$	-7.8 ± 0.6
	TBA-Br		$4.1x10^5$ ± $3.2x10^5$	-7.7 ± 0.5
	TOA-I		$1.4x10^5$	-6.9 ± 0.8
m-1^{3I}	Orthoamide	Cyclo-hexane	$5.8x10^3$	-5.1

Scheme S1: "Orthoamide" used as neutral guest for recognition titrations.



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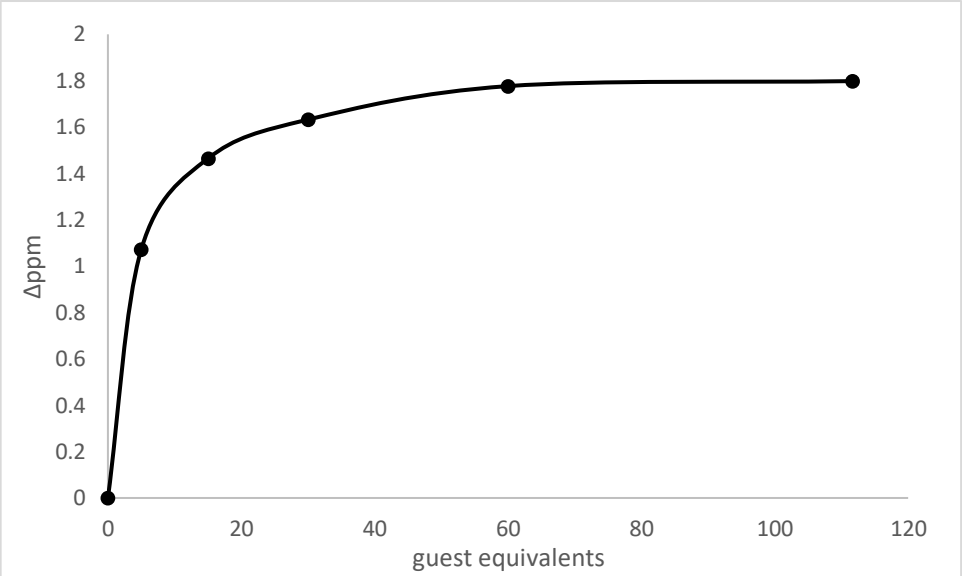

Figure S11: Titration of ***m*-5^{4Br}** with TBA-Cl.

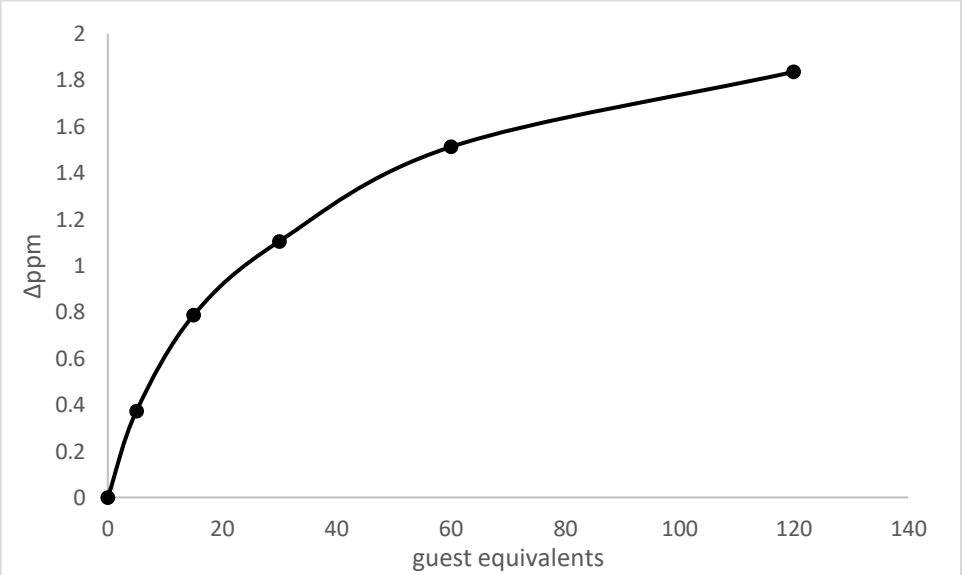

Figure S12: Titration of ***m*-5^{4Br}** with TBA-Br.

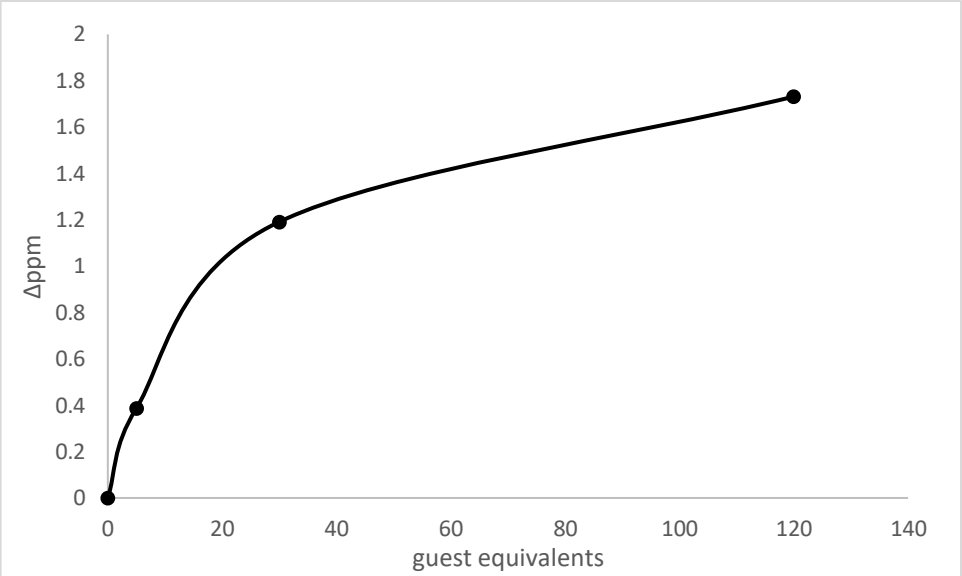

Figure S13: Titration of ***p*-5^{4Br}** with TBA-Cl.

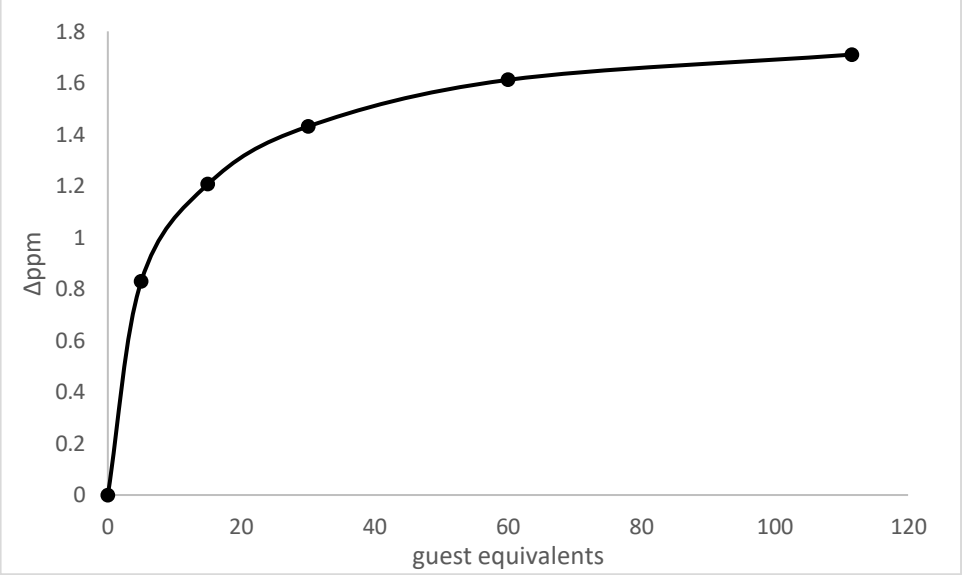

Figure S14: Titration of ***p*-5^{4Br}** with TBA-Br.

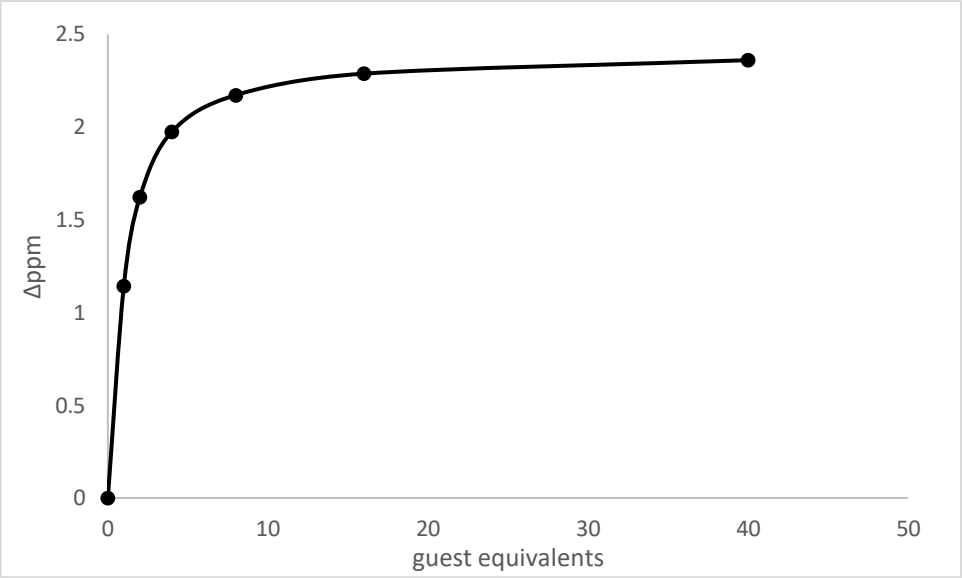

Figure S15: Titration of ***m*-5^{6Br}** with TBA-Cl.

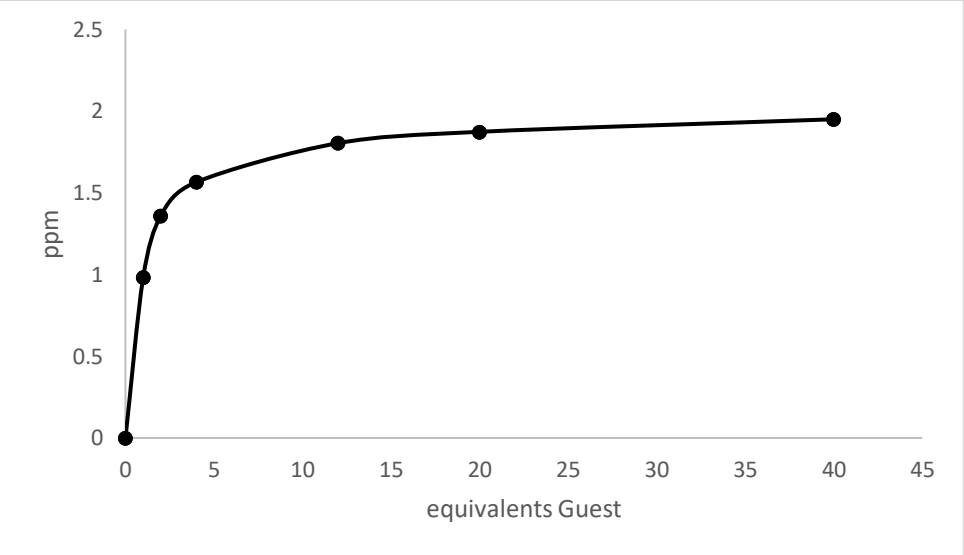

Figure S16: Titration of ***m*-5^{6Br}** with TBA-Br.

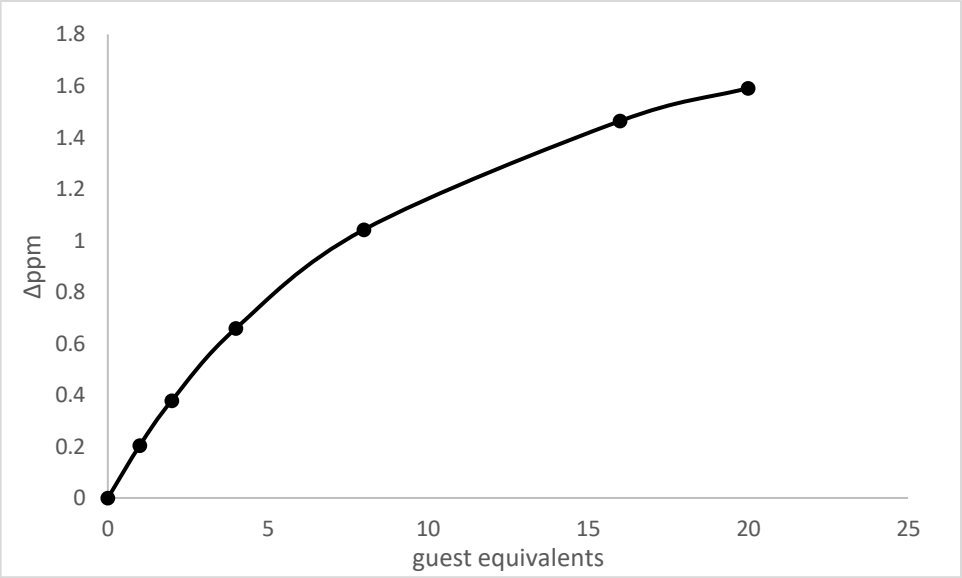

Figure S17: Titration of ***m-5^{6Br}*** with Orthoamide **6**.

E.1) DFT Calculation Data

The halogen-bonded complexes were modelled by density functional theory using M06-2X[7] functional with the triple-zeta def2-TZVPP basis set (including the corresponding pseudopotential for iodine)[8]. All geometries were fully optimized, and the nature of the minima was confirmed by the absence of relevant imaginary frequencies. Free energy values G refer to the Gibbs free energy in hartree, as provided in the Gaussian09 output.

Coordinates are provided in separate SI files (halogen bonding interactions details can be found in the manuscript)

F.) References

[1] Oxford Diffraction /Agilent Technologies UK Ltd, Agilent 2011 CrysAlis PRO, Yarnton, England.

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