Supporting Information

Experimental Procedures

Methods: Gas chromatography coupled mass spectrometry (GC-MS) was carried out on Agilent Technologies 6890N Network GC-system (Agilent, Palo Alto, CA, USA) GC with the Agilent Technologies 5975 inert MS detection and autosampler (Agilent). The injection temperature was set to 275 °C. Separation was performed on a CP-Sil 8 capillary column (50 m × 0.25 mm I.D., 0.25 μm film thickness). Helium was used as the carrier gas at a flow of 1.2 mL/min. The split was opened after 2 min. The column temperature for the CP Sil-8 was programmed from 45^{o}C to 245^{o}C with 20^{o}C/min. The final temperature was held for 10 minutes. Detection was based on electron ionization (EI) in the full scan mode (*m/z* 50-500). Nitrogen was used as reagent gas at a flow rate of 3 mL/min. The ion source temperature was 230^{o}C.

^{1}H, ^{13}C and ^{19}F NMR spectra recorded on 300 MHz NMR spectrometer (Bruker, Billerica, MA, USA), using chloroform-D ($CDCl_3$) as the solvent. The processing parameters were 300 MHz for ^{1}H, 75.5 MHz for ^{13}C and 282 for ^{19}F and a digital resolution of 0.20 Hz for ^{1}H, 0.61 Hz for ^{13}C and 0.65 Hz for ^{19}F.

Electrospray ionization (ESI) (*m/z* 100.0-1000.0) of the salts was performed as flow injection analysis on a Thermo (Waltham, Massachusetts, USA) LCQ Deca quadrupole ion trap MS. The mobile phases used were 0.1% formic acid and methanol. The gradient was started at 90% water and over 25 min went to 5% solvent water.

Table S1: ^{1}H NMR chemical shifts δ [ppm] and couplings ^{n}J (^{1}H^{1}H, ^{1}H^{19}F) [Hz] of F-PBDEs 35-F5' **(3d),** 47-F3 **(3g),** 99-F3' **(3i)**, PBDEs 35 **(3d)**, 47 **(3f)** and 99 **(3h)** in $CDCl_3$.

BZ/BZL	**#**	**Chemical shifts δ [ppm] and ^{1}H^{1}H, ^{1}H^{19}F couplings J [Hz]**
17-F5'	**3a**	δ *7.80* (H-3, 1H, *d*, $^{4}J_{H,H}$=2.3Hz), *7.59* (H-3', 1H, *dd*, $^{3}J_{H,H}$=8.8Hz, $^{4}J_{H,F}$=5.9Hz), *7.42* (H-5, 1H, *dd*, $^{3}J_{H,H}$=8.7Hz, ^{4}J=2.3Hz), *6.81* (H-6, 1H, *d*, $^{3}J_{H,H}$=8.7Hz), *6.78* (H-4', 1H, *ddd*, $^{3}J_{H,H}$=8.8Hz, $^{3}J_{H,F}$=7.7Hz, $^{4}J_{H,H}$=2.8Hz), *6.52* (H-6', 1H, *dd* , $^{3}J_{H,F}$=9.3Hz, $^{4}J_{H,H}$=2.8Hz);
25-F5'	**3b**	δ *7.79* (H-3, 1H, *d*, $^{4}J_{H,H}$=2.3Hz), *7.43* (H-5, 1H, *dd*, $^{3}J_{H,H}$=8.6Hz, $^{4}J_{H,H}$=2.3Hz), *6.99* (H4', 1H, *ddd*, $^{3}J_{H,F}$=7.9Hz, $^{4}J_{H,H}$=2.2Hz, $^{4}J_{H,H}$=1.7Hz), *6.94* (H6, 1H, *d*, $^{3}J_{H,H}$=8.6Hz), *6.84* (H2', 1H, *ddd*, $^{4}J_{H,H}$=2.2Hz, $^{4}J_{H,H}$=1.7Hz $^{5}J_{H,F}$=1.3Hz);
28-F3'	**3c**	δ *7.78* (H-3, 1H, *d*, $^{4}J_{H,H}$=2.3Hz), *7.46* (H-5', 1H, *dd*, $^{3}J_{H,H}$=8.8Hz, $^{4}J_{H,F}$=7.0Hz), *7.42* (H-5, 1H, *dd*, $^{3}J_{H,H}$=8.6Hz, $^{4}J_{H,H}$=2.3Hz), *6.91* (H-6, 1H, *d*, $^{4}J_{H,H}$=2.3), *6.71* (H-2', 1H, *dd*, $^{3}J_{H,F}$=9.4Hz, $^{4}J_{H,H}$=2.8Hz), *6.63* (H-6', 1H, *ddd*, $^{3}J_{H,H}$=8.8Hz, $^{4}J_{H,H}$=2.8Hz, $^{5}J_{H,F}$=1.1Hz);
35	**3d**	δ *7.57* (H5, 1H, *d*, $^{3}J_{H,H}$=8.8Hz), *7.30* (H4', 1H, *ddd*, $^{3}J_{H,H}$=8.0Hz, $^{4}J_{H,H}$=1.7Hz, $^{4}J_{H,H}$=1.3Hz), *7.27* (H-2, 1H, *d*, $^{4}J_{H,H}$=2.8Hz), *7.26* (H-5', 1H, *dd*, $^{3}J_{H,H}$=8.0Hz, $^{3}J_{H,H}$=7.6Hz), *7.16* (H-2', 1H, *dd*, $^{4}J_{H,H}$=2.4Hz, $^{4}J_{H,H}$=1.7Hz), *6.95* (H-6', 1H, *ddd*, $^{3}J_{H,H}$=7.6Hz, $^{4}J_{H,H}$=2.4Hz, $^{4}J_{H,H}$=1.3Hz), *6.84* (H-6, 1H, *dd*, $^{3}J_{H,H}$=8.8Hz, $^{4}J_{H,H}$=2.8Hz);
35-F5'	**3e**	δ *7.61* (H-5, 1H, *d*, $^{3}J_{H,H}$=8.8Hz,), *7.31* (H-2, 1H, *d*, $^{4}J_{H,H}$=2.8Hz), *7.04* (H-4', 1H, *ddd*, $^{3}J_{H,F}$=7.9Hz, $^{4}J_{H,H}$=2.2Hz, $^{4}J_{H,H}$=1.7Hz), *6.93* (H-2', 1H, *ddd*, $^{4}J_{H;H}$=2.2Hz, $^{4}J_{H;H}$=1.7Hz, $^{5}J_{H,F}$=1.2Hz), δ *6.88* (H-6, 1H, *dd*, ^{3}J=8.8Hz, ^{4}J=2.8Hz), *6.66* (H-6', 1H, *dt*, $^{3}J_{H,F}$=9.6Hz, $^{4}J_{H,2H}$=2.2Hz);
47	**3f**	δ *7.79* (H-3/3', 2H, *d*, ^{4}J=2.3Hz), *7.38* (H5/5', 2H, *dd*, ^{3}J=8.7Hz, ^{4}J=2.3Hz), *6.72* (H6/6', 2H, *d*, ^{3}J=8.7);
47-F3	**3g**	δ *7.81* (H-3', 1H, *d*, $^{4}J_{H,H}$=2.3Hz), *7.43* (H-5, 1H, *dd*, $^{3}J_{H,H}$=8.9Hz, $^{4}J_{H,F}$=7.4Hz), *7.42* (H-5', 1H, *dd*, $^{3}J_{H,H}$=8.6, $^{4}J_{H,H}$=2.3), *6.82* (H-6', 1H, *d*, $^{3}J_{H,H}$=8.6Hz), *6.48* (H-6, 1H, *dd*, $^{3}J_{H,H}$=8.9Hz, $^{5}J_{H,F}$=1.8Hz);
99	**3h**	δ *7.89* (H-3, 1H, *s*), *7.81* (H-3', 1H, *d*, $^{4}J_{H,H}$=2.3Hz), *7.43* (H-5', 1H, *dd*, $^{3}J_{H,H}$=8.7Hz, $^{4}J_{H,F}$=2.3Hz), *6.98* (H-6, 1H, *s*), *6.81* (H-6', 1H, *d*, $^{3}J_{H,H}$=8.7Hz);
99-F3'	**3i**	δ *7.90* (H-3, 1H, *s*), *7.49* (H-5', 1H, *dd*, $^{3}J_{H,H}$=8.9Hz, $^{4}J_{H,F}$=7.3Hz), *7.10* (H-6, 1H, *s*), δ *6.59* (H-6', 1H, *dd*, $^{3}J_{H,H}$=8.9Hz, $^{5}J_{H,F}$=1.8Hz);

Table S2: ^{19}F NMR chemical shifts δ [ppm] and couplings ^{n}J (^{1}H^{1}H, ^{1}H^{19}F) [Hz] of F-PBDEs 35-F5’ **(3d),** 47-F3 **(3g),** 99-F3’ **(3i)**, PBDEs 35 **(3d)**, 47 **(3f)** and 99 **(3h)** in $CDCl_3$.

BZL	#	δ **[ppm]**	**multiplicity**	^{3}J**(F,H)**	^{4}J**(F,H)**	^{5}J**(F,H5)**
17-F5'	**3a**	-111.33	*ddd*	H-6'=9.3, H-4'=7.7	H-3'=5.9	
25-F5'	**3b**	-108.88	*ddd*	H-6'=9.7, H-4'=7.9		H-2'=1.7
28-F3'	**3c**	-103.86	*ddd*	H-2'=9.4	H-5'=7.0	H-6'=1.1
35-F5'	**3e**	-108.73	*ddd*	H-6'=9.6, H-4'=7.9		H-2'=1.2
47-F3	**3g**	- 95.27	*dd*		H-5=7.4	H-6=1.8
99-F3'	**3i**	- 94.68	*dd*		H-5‘=7.3	H-6‘=1.8

Table S3: ^{13}C NMR chemical shifts δ [ppm] and couplings ^{n}J (^{13}C^{19}F) [Hz] of F-PBDEs 35-F5' **(3d),** 47-F3 **(3g),** 99-F3' **(3i)**, PBDEs 35 **(3d)**, 47 **(3f)** and 99 **(3h)** in $CDCl_3$.

BZ/BZL	**#**	**C-1**	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**
17-F5'	**3a**	152.03	115.85	136.59	117.92	132.08	121.61
25-F5'	**3b**	151.40	116.88	136.64	118.67	132.29	123.33
28-F3'	**3c**	151.79	116.60	136.55	118.29	132.19	122.90
35	**3d**	156.48	124.22	125.63	119.10	134.55	119.49
35-F5'	**3e**	155.42	120.06	125.85	120.12	134.74	124.92
47	**3f**	152.48	115.38	136.52	117.70	131.96	120.77
47-F3	**3g**	154.20	103.23	157.13	104.18	132.12	114.53
99	**3h**	153.02	115.82	137.58	119.93	124.38	123.06
99-F3'	**3i**	152.46	114.01	137.72	120.79	124.52	124.11

BZ/BZL	#	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
17-F5'	**3a**	154.10	108.36	134.63	112.49	162.53	106.88
25-F5'	**3b**	158.62	116.48	123.23	114.32	163.43	104.31
28-F3'	**3c**	157.30	106.53	159.65	102.78	134.04	114.41
35	**3d**	157.21	122.53	123.29	127.50	131.32	117.94
35-F5'	**3e**	158.04	117.83		114.93		105.61
47	**3f**	152.48	115.38	136.52	117.70	131.96	120.77
47-F3	**3g**	151.92	115.94	136.66	118.19	132.14	121.77
99	**3h**	151.77	113.48	136.74	118.29	132.22	121.65
99-F3'	**3i**				105.10	132.36	115.43

BZL#	#	^{1}J(F,C)	^{2}J(F,C)	^{3}J(F,C)	^{4}J(F,C)
17-F5'	**3a**	C5'=249.0	C4'=22.5;C6'=26.1	C1'=10.1;C3'=9.2	C2'=4.7
25-F5'	**3b**	C5'=251.5	C4'=24.7;C6'=25.2	C1'=11.7;C3'=8.6	C2'=3.4
28-F3'	**3c**	C3'=249.2	C2'=25.8;C4'=21.2	C1'=9.5;C3'=1.6	C6'=3.5
35-F5'	**3e**		C4'=23.4;C6'=25.7		C2'=3.5
47-F3	**3g**	C3=246.9	C2=24.2; C4=22.7	C1=12.5; C5=11.3	C6=3.8
99-F3'	**3i**		C4'=22.8		C6'=3.8

Table S4: *m/z* values and relative abundance [%] of ions of 2,2',4,4'-tertrabromo-diphenyl iodonium salt **(1a)**, 3,3',4,4'-tertrabromo-diphenyl iodonium salt **(1b)** and 2,2',4,4',5,5'-hexabromo-diphenyl iodonium salt **(1c)** measured by HPLC-MS.

Iodonium salt #	**$[^{13}C\ M]^+$**		**$[M]^{+\cdot}$**		**$[M\text{-}HBr]^+$**		**$[M\text{-}I]^+$**		**$[M\text{-}Br_2]^+$**		**$[M\text{-}IBr]^+$**		**$[C_6H_3IBr_2]^{+\cdot}$**		**$[M\text{-}IBr_x]^+$**		**$[M]^{++}$**		**$[C_6H_4Br_2O]^+$**	
1a	*602*	2	*601*	15	*521*	2	*474*	3	*439*	4	*393*	5	*364*	21	*312*	14	*301*	2	*254*	7
	600	8	*599*	61	*519*	7	*472*	9	*437*	8	*391*	16	*362*	43	*310*	25	*300*	12	*252*	11
	598	12	*597*	100	*517*	9	*470*	14	*435*	4	*389*	16	*360*	20	*308*	13	*299*	2	*250*	7
	596	9	*595*	67	*515*	3	*468*	10			*387*	6			X=		*298*	12		
															2					
	594	2	*593*	16			*466*	3												
1b	*602*	2	*601*	16	*521*	3	*474*	12	*439*	1	*393*	1	*364*	4	*312*	19	*301*	1	*254*	9
	600	10	*599*	66	*519*	9	*472*	52	*437*	2	*391*	2	*362*	7	*310*	33	*300*	2	*252*	18
	598	13	*597*	100	*517*	10	*470*	77	*435*	1	*389*	2	*360*	3	*308*	19	*299*	2	*250*	9
	596	9	*595*	67	*515*	4	*468*	54			*387*	1			X=					
	594	2	*593*	17			*466*	13							2					
1c	*762*	1	*761*	4	*681*	2	*634*	1	*601*	1	*553*	2	--		*444*	7	*381*	1	*254*	7
	760	4	*759*	26	*679*	3	*632*	3	*599*	1	*551*	7	--		*442*	20	*380*	8	*252*	15
	758	9	*757*	70	*677*	5	*630*	5	*597*	1	*549*	19	--		*440*	21	*379*	2	*250*	8
	756	12	*755*	100	*675*	1	*628*	7			*547*	19			*438*	7		6		
	754	9	*753*	76			*626*	6			*545*	8			X=					
	752	4	*751*	31			*624*	4			*543*	2			3					
	750	1	*749*	5			*622*	1												

Table S5: *m/z* values and relative abundance [%] of ions of PBDEs and F-PBDEs **(3a-i)** measured by GC-MS.

BZ/BLZ#	#	[^{13}C M]$^{+\cdot}$		[M]$^{+\cdot}$		[M-Br$_2$+1]$^{+\cdot}$		[M-Br$_2$]$^{+\cdot}$		[C$_{11}$(F)H$_x$]$^{+\cdot}$	
17F-5'	**3a**	429	2	428	20	265	15	264	100	157	43
		427	7	426	58	267	12	266	97	F;	
		425	8	424	58					x=6	
		423	3	422	21						
25F-5'	**3b**	429	1	428	10	267	15	266	100	157	33
		427	4	426	31	265	12	264	95	F;	
		425	4	424	30					x=6	
		423	1	422	11						
28F-3'	**3c**	429	2	428	15	267	11	266	98	157	49
		427	6	426	47	265	15	264	100	F;	
		425	6	424	47					x=6	
		423	2	422	17						
35	**3d**	411	3	410	31	249	4	248	30	139	50
		409	13	408	97	247	5	246	33	x=7	
		407	13	406	100						
		405	4	404	35						
35F-5'	**3e**	429	3	428	33	267	5	266	41	157	66
		427	13	426	100	265	7	264	43	F;	
		425	13	424	99					x=6	
		423	4	422	37						
47	**3f**	491	2	490	17	329	6	328	42	138	11
		489	8	488	65	327	12	326	87	x=6	
		487	14	486	100	325	7	324	46		
		485	9	484	70						
		483	0	482	18						
47F-3	**3g**	509	2	508	13	347	6	346	48	156	18
		507	6	506	50	345	12	344	100	F;	
		505	10	504	77	343	8	342	50	x=5	
		503	6	502	52						
		502	2	500	14						
99	**3h**	571	1	570	7	409	4	408	31	137	21
		569	4	568	35	407	12	406	95	x=5	
		567	8	566	69	405	13	404	100		
		565	9	564	71	403	5	402	33		
		563	4	562	37						
		561	1	560	7						
99F-3'	**3i**	589	1	588	7	427	4	426	31	155	23
		587	4	586	32	425	12	424	91	F;	
		585	8	584	64	423	13	422	100	x=4	
		583	9	582	67	421	5	420	35		
		581	4	580	34						
		579	1	578	7						