Diazaborolyl-boryl push-pull systems with ethynylene-arylene bridges as 'turn-on' fluoride sensors.

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Contents

		3	**12**	**20**
cyclohexane	λ_{abs} [nm]	342	374	344
	λ_{em} [nm]	421	441	429
	ε [$Lmol^{-1}cm^{-1}$]	21300	22500	22200
	Φ_{fl}	0.99	0.83	0.94
toluene	λ_{abs} [nm]	343	369	343
	λ_{em} [nm]	458	473	454
	ε [$Lmol^{-1}cm^{-1}$]	17000	25200	37200
	Φ_{fl}	0.71	0.72	0.72
THF	λ_{abs} [nm]	342	374	343
	λ_{em} [nm]	503	516	495
	ε [$Lmol^{-1}cm^{-1}$]	18800	24900	38200
	Φ_{fl}	0.02	0.05	0.03
CH_2Cl_2	λ_{abs} [nm]	342	368	344
	λ_{em} [nm]	511	525	505
	ε [$Lmol^{-1}cm^{-1}$]	22600	18600	34300
	Φ_{fl}	0.47	0.49	0.50
CH_3CN	λ_{abs} [nm]	335	354	334
	λ_{em} [nm]	391 / 550	394 / 567	342 / 546
	ε [$Lmol^{-1}cm^{-1}$]	9700	23000	4500
	Φ_{fl}	0.16 / 0.03	0.13 / 0.08	0.02 / 0.06

Table S1: Absorption- and emission maxima of **3**, **12**, and **20** in different solvents.

		[3·F]$^-$	**[12·F]$^-$**	**[20·F]$^-$**	**[20·2F]$^{2-}$**
cyclohexane	λ_{abs} [nm]	308	331	316	312
	λ_{em} [nm]	353	382	380	380
toluene	λ_{abs} [nm]	310	334	318	312
	λ_{em} [nm]	353	384	396	389
THF	λ_{abs} [nm]	310	334	318	313
	λ_{em} [nm]	393	384	408	401
CH_2Cl_2	λ_{abs} [nm]	312	334	316	313
	λ_{em} [nm]	399	390	407	407

Table S2: Absorption and emission maxima of **[3·F]$^-$**, **[12·F]$^-$**, **[20·F]$^-$** and **[20·2F]$^{2-}$** in different solvents.

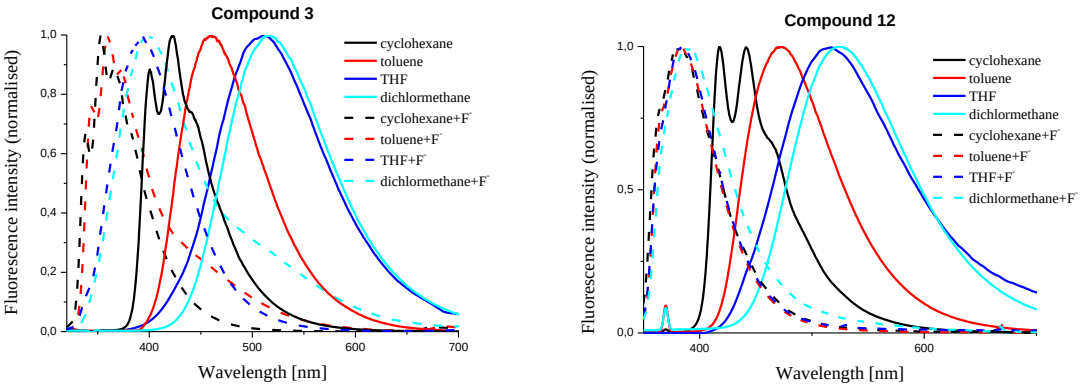


Figure S1: Emission spectra of **3**, **[3·F]**$^-$, **12** and **[12·F]**$^-$ in different solvents.

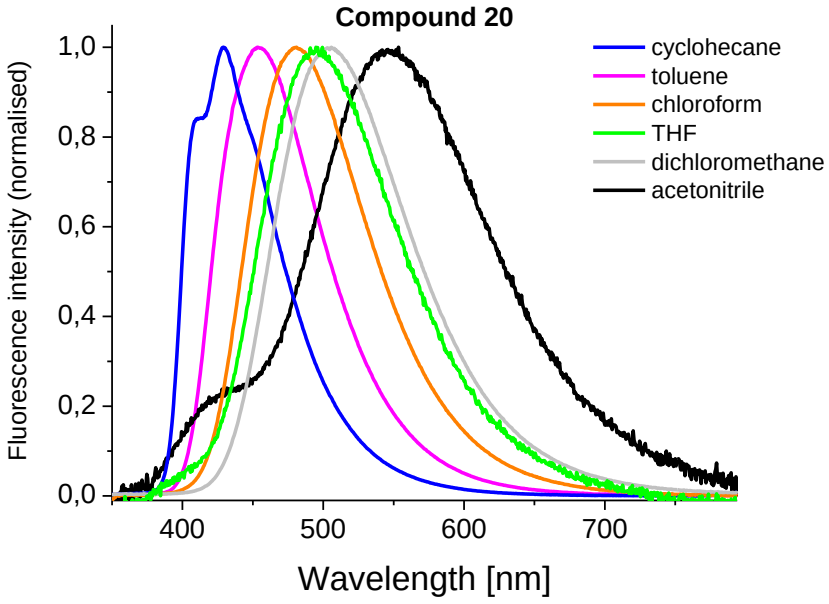


Figure S2: Emission spectra of **20** in different solvents.

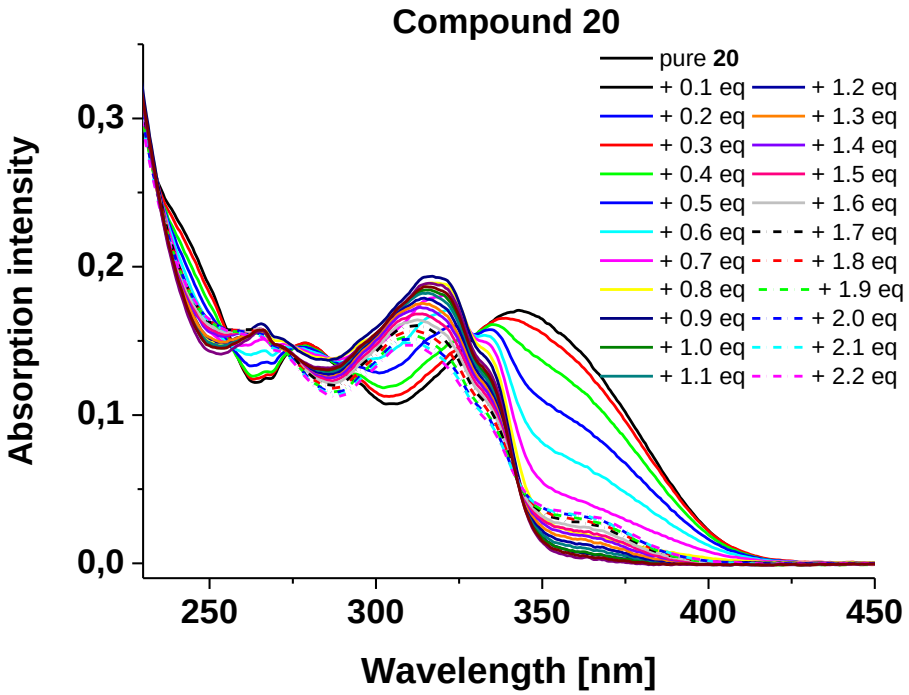


Figure S3: Absorption titration of **20** with TBAF in THF.

	3			**12**			**[12·F]$^-$**		
Bond lengths (Å)		exp.	calc.		exp.	calc.		exp.[a]	calc.
B−N	B(1)-N(1) B(1)-N(2)	1.425(3) 1.427(3)	1.439 1.439	B(1)-N(1) B(1)-N(2)	1.425(3) 1.422(3)	1.439 1.438	B(1)-N(1) B(1)-N(2)	1.422(3) 1.427(3)	1.447 1.448
B−C	B(1)-C(11) B(2)-C(16) B(2)-C(19) B(2)-C(28)	1.528(3) 1.565(3) 1.581(3) 1.578(3)	1.517 1.571 1.585 1.585	B(1)-C(11) B(2)-C(16) B(2)-C(17) B(2)-C(26)	1.520(3) 1.541(3) 1.579(3) 1.578(3)	1.516 1.550 1.586 1.585	B(1)-C(11) B(2)-C(16) B(2)-C(17) B(2)-C(26)	1.533(3) 1.646(3) 1.667(3) 1.648(3)	1.502 1.656 1.673 1.669
B−Hal							B(2)-F(1)	1.477(2)	1.454
C−C	C(11)-C(12) C(12)-C(13) C(13)-C(14) C(14)-C(15) C(15)-C(16) C(16)-C(17) C(17)-C(18) C(13)-C(18)	1.205(3) 1.437(2) 1.398(3) 1.390(3) 1.403(3) 1.401(3) 1.381(3) 1.402(3)	1.221 1.424 1.411 1.389 1.412 1.412 1.389 1.411	C(11)-C(12) C(12)-C(13) C(13)-C(14) C(14)-C(15) C(15)-C(16)	1.207(3) 1.425(3) 1.371(3) 1.404(3) 1.375(3)	1.223 1.406 1.390 1.409 1.391	C(11)-C(12) C(12)-C(13) C(13)-C(14) C(14)-C(15) C(15)-C(16)	1.211(3) 1.422(3) 1.378(3) 1.411(3) 1.383(3)	1.227 1.400 1.388 1.413 1.387
C−N	N(1)-C(1) N(2)-C(2) N(1)-C(7) N(2)-C(9)	1.395(2) 1.401(2) 1.455(2) 1.463(2)	1.395 1.395 1.456 1.456	N(1)-C(1) N(2)-C(2) N(1)-C(7) N(2)-C(9)	1.392(2) 1.391(2) 1.460(3) 1.462(3)	1.395 1.395 1.457 1.457	N(1)-C(1) N(2)-C(2) N(1)-C(7) N(2)-C(9)	1.396(3) 1.396(3) 1.463(3) 1.459(3)	1.392 1.392 1.455 1.454
C−S				S(1)-C(13) S(1)-C(16)	1.711(2) 1.722(2)	1.748 1.755	S(1)-C(13) S(1)-C(16)	1.734(2) 1.732(2)	1.763 1.743
Bond Angles (°)									
C−C−C	C(11)-C(12)-C(13)	178.8(2)	180.0	C(11)-C(12)-C(13)	178.2(3)	179.2	C(11)-C(12)-C(13)	178.7(2)	179.2
B−C−C	B(1)-C(11)-C(12)	177.8(2)	179.9	B(1)-C(11)-C(12)	176.4(2)	179.7	B(1)-C(11)-C(12)	173.5(2)	179.9

[a] Bond lengths and bond angles of all four independent molecules in the unit cell were essentially identical within 3 esds. Thus only data of molecule **A** are shown here.

Table S3: Comparison of experimental and calculated geometric parameters of **3**, **12** and **[12·F]$^-$**.

MO-number		eV	Borole	Bridge	B-boryl	Mes-groups
144	L+3	0.01	0	8	3	89
143	L+2	-0.13	0	87	0	13
142	L+1	-0.66	20	34	14	32
141	LUMO	-1.97	6	46	31	16
140	HOMO	-5.24	83	16	1	1
139	H-1	-5.82	100	0	0	0
138	H-2	-6.03	0	4	1	94
137	H-3	-6.12	2	6	2	90

Table S4: Molecular orbital contributions of compound **3**. Co-planar geometry.

MO-number		eV	Borole	Bridge	B-boryl	Mes-groups
145	L+3	0.16	6	22	0	72
144	L+2	0.00	0	6	3	91
143	L+1	-0.69	18	38	16	28
142	LUMO	-2.1	7	55	26	12
141	HOMO	-5.24	77	21	1	2
140	H-1	-5.86	100	0	0	0
139	H-2	-6.06	5	11	1	83
138	H-3	-6.07	4	10	1	85

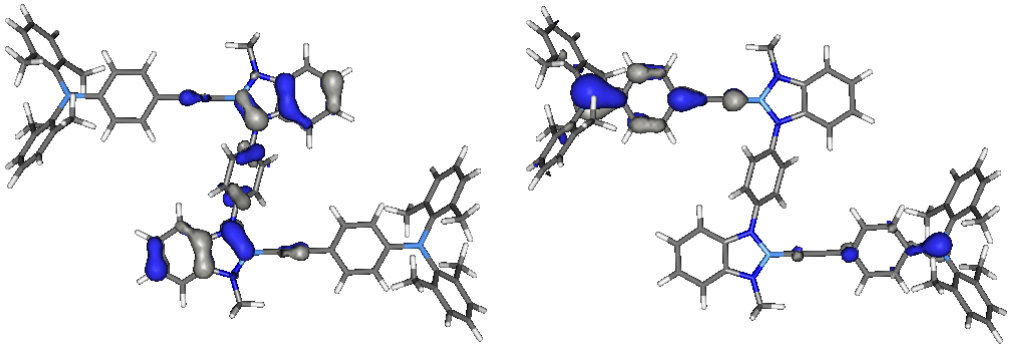
Table S5: Molecular orbital contributions of compound **12**. Co-planar geometry.

MO-number		eV	$C_6H_4(NEt)_2$	B-Borole	Bridge	$BMes_2F$
149	L+3	2.98	0	0	81	19
148	L+2	2.41	100	0	0	0
147	L+1	2.25	72	0	26	1
146	LUMO	1.33	31	18	50	2
145	HOMO	-2.59	1	0	14	85
144	H-1	-2.72	0	0	1	99
143	H-2	-2.84	14	0	50	35
142	H-3	-2.97	1	0	3	96

Table S6: Molecular orbital contributions of compound **[3·F]$^-$**. Co-planar geometry.

MO-number		eV	$C_6H_4(NEt)_2$	B-Borole	Bridge	$BMes_2F$
150	L+3	2.94	9	11	76	5
149	L+2	2.51	100	0	0	0
148	L+1	2.29	75	0	24	1
147	LUMO	1.36	25	16	57	2
146	HOMO	-2.49	13	0	65	21
145	H-1	-2.71	2	0	11	87
144	H-2	-2.77	1	0	2	97
143	H-3	-3.02	0	0	1	99

Table S7: Molecular orbital contributions of compound **[12·F]**$^-$. Co-planar geometry.



HOMO
-5.54 eV

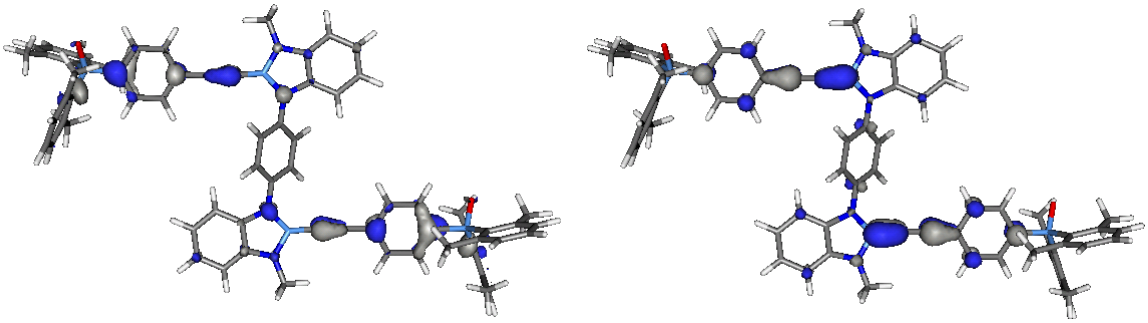
HLG
3.18 eV

LUMO
-2.36 eV

Figure S4: Frontier orbitals of **20′**.

MO-number		eV	Borolyl-π-borylunit 1	Borolyl-π-borylunit 2	C_6H_4-Spacer
270	L+10	-0.29	24	36	40
269	L+9	-0.46	55	44	1
268	L+8	-0.46	43	55	3
267	L+7	-0.57	16	10	74
266	L+6	-0.62	81	0	19
265	L+5	-0.62	0	89	10
264	L+4	-0.70	19	18	64
263	L+3	-1.08	49	51	0
262	L+2	-1.12	49	47	4
261	L+1	-2.34	69	30	0
260	LUMO	-2.36	30	69	1
259	HOMO	-5.54	43	42	15
258	H-1	-5.71	49	50	1
257	H-2	-6.02	42	43	16
256	H-3	-6.33	49	47	4
255	H-4	-6.48	0	100	0
254	H-5	-6.49	100	0	0
253	H-6	-6.52	100	0	0
252	H-7	-6.52	0	100	0
251	H-8	-6.58	100	0	0
250	H-9	-6.59	0	100	0
249	H-10	-6.61	97	3	0

Table S8: Molecular orbital contributions of **20′**.



HOMO
-2.16 eV

HLG
4.04 eV

LUMO
1.88 eV

Figure S5: Frontier orbitals of **[20′·2F]**$^{2-}$.

MO-number		eV	Borolyl-π-borate unit 1	Borolyl-π-borate unit 2	C_6H_4-Spacer
280	L+10	3.05	59	44	-2
279	L+9	2.99	114	64	-77
278	L+8	2.98	48	48	4
277	L+7	2.94	37	63	0
276	L+6	2.83	48	47	5
275	L+5	2.54	-3	-3	108
274	L+4	2.52	6	6	89
273	L+3	2.47	-4	-4	110
272	L+2	2.31	20	19	62
271	L+1	1.95	48	52	0
270	LUMO	1.88	50	45	5
269	HOMO	-2.16	49	47	4
268	H-1	-2.21	48	51	0
267	H-2	-2.34	24	74	2
266	H-3	-2.37	75	25	0
265	H-4	-2.44	0	100	0
264	H-5	-2.46	100	0	0
263	H-6	-2.56	1	99	0
262	H-7	-2.58	99	1	0
261	H-8	-2.60	0	100	0
260	H-9	-2.63	100	0	0
259	H-10	-2.80	42	40	18

Table S9: Molecular orbital contributions of **[20′·2F]**$^{2-}$.

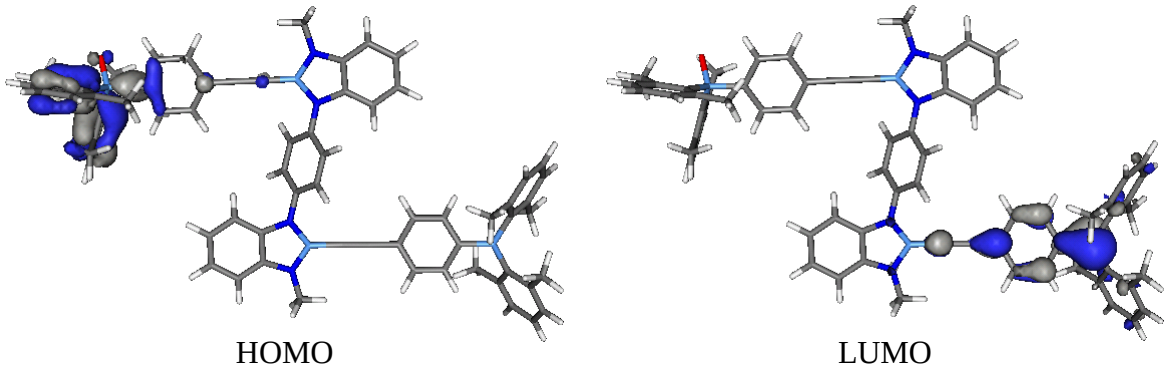


Figure S6: Frontier orbitals of **[20′·F]**$^{-}$.

MO-number		eV	Borolyl-π-borylunit	Borolyl-π-borate unit	C_6H_4-Spacer
275	L+10	0.97	72	7	21
274	L+9	0.94	60	0	41
273	L+8	0.87	15	27	58
272	L+7	0.74	60	34	6
271	L+6	0.72	70	20	10
270	L+5	0.71	63	29	8
269	L+4	0.59	100	0	0
268	L+3	0.40	100	0	0
267	L+2	0.38	100	0	0
266	L+1	-0.04	99	0	1
265	LUMO	-1.37	100	0	0
264	HOMO	-3.10	0	100	0
263	H-1	-3.25	0	100	0
262	H-2	-3.31	0	99	1
261	H-3	-3.39	0	100	0
260	H-4	-3.43	0	100	0
259	H-5	-3.96	4	89	7
258	H-6	-4.22	47	39	15
257	H-7	-4.24	3	96	1
256	H-8	-4.35	8	91	0
255	H-9	-4.47	34	60	5
254	H-10	-4.53	16	79	4

Table S10: Molecular orbital contributions of **[20′·F]**$^{-}$.

	Obs.	Calc. B3LYP			Calc. CAM-B3LYP		
	λ_{max} (eV)	λ_{max} (eV)	Osc. Str.	Major transition (κ_{ia})	λ_{max}(eV)	Osc. Str.	Major transitions
3	3.63	2.98	0.0006	HOMO → LUMO (0.70)	3.98	0.1139	HOMO-2 → LUMO (0.66)
12	3.34	2.89	0.0000	HOMO → LUMO (0.70)	3.85	0.7165	HOMO-2 → LUMO (0.68)
[3·F]$^-$	4.03	3.74	0.0010	HOMO-2 → LUMO (0.40) HOMO → LUMO (0.52)	4.46	0.0010	HOMO → LUMO+3 (0.27) HOMO-2 → LUMO (0.47)
[12·F]$^-$	3.75	3.33	0.0002	HOMO → LUMO (0.64)	3.91	0.0004	HOMO → LUMO+3 (0.29) HOMO → LUMO (0.53)

Table S11: TD-DFT data for the first vertical excitation for perpendicular geometries using B3LYP and CAM-B3LYP functionals

MO-number		eV	Borole	Bridge	Boryl-B	Mes-groups
144	L+3	-0.14	0	88	0	12
143	L+2	-0.30	60	35	1	4
142	L+1	-0.43	8	46	9	37
141	LUMO	-1.91	1	45	35	19
140	HOMO	-5.30	92	8	0	0
139	H-1	-5.80	100	0	0	0
138	H-2	-6.04	0	4	1	94
137	H-3	-6.09	1	30	1	68

Table S12: Molecular orbital contributions of compound **3**. Perpendicular geometry.

MO-number		eV	Borole	Bridge	Boryl-B	Mes-groups
145	L+3	0.00	0	5	3	92
144	L+2	-0.45	11	46	12	32
143	L+1	-0.58	46	47	2	6
142	LUMO	-2.01	2	55	30	14
141	HOMO	-5.36	92	8	0	0
140	H-1	-5.85	100	0	0	0
139	H-2	-5.93	2	57	1	41
138	H-3	-6.07	0	4	1	94

Table S13: Molecular orbital contributions of compound **12**. Perpendicular geometry.

MO-number		eV	$C_6H_4(NEt)_2$	Borole-B	Bridge	$BMes_2F$
149	L+3	2.65	57	15	28	0
148	L+2	2.37	100	0	0	0
147	L+1	2.04	4	5	88	4
146	LUMO	1.56	59	21	20	0
145	HOMO	-2.56	0	0	12	88
144	H-1	-2.69	0	0	1	99
143	H-2	-2.87	1	0	49	50
142	H-3	-2.96	0	0	11	88

Table S14: Molecular orbital contributions of compound **[3·F]**$^-$. Perpendicular geometry.

MO-number		eV	$C_6H_4(NEt)_2$	Borole-B	Bridge	$BMes_2F$
150	L+3	2.60	62	10	28	1
149	L+2	2.43	100	0	0	0
148	L+1	1.96	3	4	90	3
147	LUMO	1.55	52	22	26	0
146	HOMO	-2.50	1	1	67	31
145	H-1	-2.68	0	0	16	83
144	H-2	-2.73	0	0	5	95
143	H-3	-2.98	0	0	1	99

Table S15: Molecular orbital contributions of compound **[12·F]**$^-$. Perpendicular geometry.