Azulene-Boronate Esters: Colorimetric Indicators for Fluoride in Drinking Water

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ELECTRONIC SUPPLEMENTARY INFORMATION

Computational Supporting Information

Computational Details / Methodology

DFT calculations were run with Gaussian 09 (Revision D.01),[1] all atoms were described with the 6-31G** basis set (BS1).[2] Initial BP86[3] optimizations were performed using the 'grid = ultrafine' option, with all stationary points being fully characterized via analytical frequency calculations as minima (all positive eigenvalues). All energies were recomputed with a larger basis set; 6-311++G** (BS2). Corrections for the effect of THF (ε = 7.4257) solvent were run using the polarizable continuum model and BS1.[4] Single-point dispersion corrections to the BP86 results employed Grimme's D3 parameter set with Becke-Johnson damping as implemented in Gaussian.[5]

Breakdown of Energy Contributions

The following tables detail the evolution of the relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

$\mathbf{\Delta E_{BS1}}$	SCF energy computed with the BP86 functional with BS1
$\mathbf{\Delta H_{BS1}}$	Enthalpy at 0 K with BS1
$\mathbf{\Delta G_{BS1}}$	Free energy at 298.15 K and 1 atm with BS1
$\mathbf{\Delta G_{BS1/THF}}$	Free energy corrected for THF with BS1
$\mathbf{\Delta G_{BS1/THF+D3}}$	Free energy corrected for THF and dispersion effects with BS1
$\mathbf{\Delta G_{THF}}$	Free energy corrected for basis set (BS2), dispersion effects and THF solvent
$\mathbf{\Delta G_{rxn}}$	Free energy (ΔG_{THF}) for the reaction of **Az-*x*-Bpin** + F^- → [**Az-*x*-Bpin**-F]$^-$
Keq	Equilibrium constant based on ΔG_{rxn} at T = 298 K to 3 significant figures

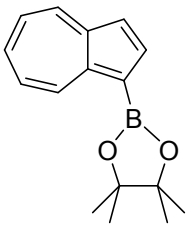
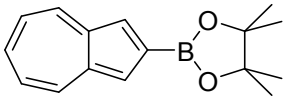
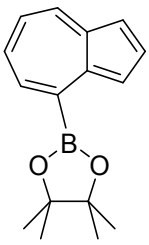
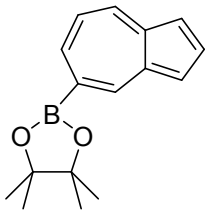
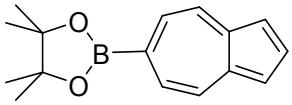
In each case the final data used in the main article is highlighted in bold.

This research made use of the Balena High Performance Computing (HPC) Service at the University of Bath.

Energy Tables

Table S1 – Computed relative energies (kcal/mol) for substituted **A** and **B** species. Data in bold are those used in the main text. Energies are quoted relative to isomer **A-2** / **B-2** for each species (or substituted species) at 0.0 kcal/mol.

	ΔE_{BS1}	ΔH_{BS1}	ΔG_{BS1}	$\Delta G_{BS1/THF}$	$\Delta G_{BS1/THF+D3}$	ΔE_{BS2}	ΔG_{THF}	ΔG_{rxn}	K_{eq}
Az-1-Bpin	-2.9	-2.6	-2.4	-2.0	-3.0	-2.3	**-2.4**		
Az-2-Bpin	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**		
Az-4-Bpin	4.1	4.1	4.2	4.6	3.1	4.7	**3.7**		
Az-5-Bpin	0.3	0.3	0.6	1.2	0.6	0.7	**0.9**		
Az-6-Bpin	1.6	1.6	1.8	2.3	1.8	2.0	**2.2**		
[Az-1-Bpin-F]$^-$	0.4	0.5	1.0	1.1	-0.1	1.2	**0.8**	**-1.9**	*26.1*
[Az-2-Bpin-F]$^-$	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	**-5.1**	*5280*
[Az-4-Bpin-F]$^-$	-0.2	-0.1	0.5	1.2	-0.4	1.1	**0.9**	**-7.9**	*608000*
[Az-5-Bpin-F]$^-$	-1.8	-1.8	-1.7	-0.1	-0.8	-1.3	**-0.3**	**-6.3**	*38700*
[Az-6-Bpin-F]$^-$	-3.2	-3.1	-3.3	-1.3	-1.8	-2.5	**-1.1**	**-8.4**	*1360000*

		
Az-1-Bpin	**Az-2-Bpin**	**Az-4-Bpin**
		
Az-5-Bpin	**Az-6-Bpin**	

Cartesian Coordinates and Computed Energies (in Hartrees)

F^-
SCF (BP86) Energy = -99.7479825386
Enthalpy 0K = -99.747983
Enthalpy 298K = -99.745622
Free Energy 298K = -99.762141
SCF (THF) Energy = -99.8716271408
SCF (BP86-D3BJ) Energy = -99.7479825386
SCF (BS2) Energy = -99.8882388026

F 0.00000 0.00000 0.00000

A-1
SCF (BP86) Energy = -796.521091207
Enthalpy 0K = -796.211663
Enthalpy 298K = -796.192908
Free Energy 298K = -796.256665
Lowest Frequency = 24.8916 cm^{-1}
Second Frequency = 44.9612 cm^{-1}
SCF (THF) Energy = -796.526418739
SCF (BP86-D3BJ) Energy = -796.594236615
SCF (BS2) Energy = -796.717713590

C -4.40466 1.73714 -0.10602
C -4.99475 0.46113 -0.03952
C -4.36358 -0.79128 0.03039
C -3.04624 2.09342 -0.11983
C -2.99394 -1.09167 0.05028
C -1.90919 1.26340 -0.07286
C -1.84057 -0.13364 0.00012
H -6.09116 0.44258 -0.04206
H -5.03374 -1.66103 0.07589
H -2.84097 3.16941 -0.17522
H -0.93745 1.77226 -0.09676
C -2.43717 -2.39207 0.12214
H -3.01247 -3.31905 0.17095
C -0.63806 -0.90702 0.04337
B 0.82437 -0.41904 0.02144
O 1.21782 0.90983 -0.12999
O 1.90295 -1.28686 0.15361
C 2.65669 0.96595 0.14424
C 3.11241 -0.52048 -0.14968
C 4.24827 -1.03855 0.73823
H 4.46996 -2.08755 0.48181
H 5.16841 -0.44896 0.58336
H 3.98012 -0.99937 1.80451
C 2.81020 1.36661 1.62251
H 3.86862 1.50409 1.90067
H 2.28173 2.31868 1.79276
H 2.36784 0.60738 2.28808
C 3.43602 -0.77264 -1.63356
H 4.38136 -0.29029 -1.93409
H 3.53302 -1.85797 -1.79823
H 2.62864 -0.40045 -2.28538
C 3.28054 2.02972 -0.76424
H 2.87772 3.02290 -0.50549
H 4.37591 2.06352 -0.63331
H 3.05891 1.83858 -1.82477
H -5.11038 2.57671 -0.15330
C -1.03605 -2.27480 0.11656
H -0.33353 -3.11132 0.16179

A-2
SCF (BP86) Energy = -796.516529378
Enthalpy 0K = -796.207458
Enthalpy 298K = -796.188640
Free Energy 298K = -796.252851
Lowest Frequency = 28.5153 cm^{-1}
Second Frequency = 35.8105 cm^{-1}
SCF (THF) Energy = -796.522494624
SCF (BP86-D3BJ) Energy = -796.588108170
SCF (BS2) Energy = -796.714099051

C 5.68739 0.00003 -0.00001
C 5.09225 -1.26974 -0.11409
C 3.72508 -1.59851 -0.14399
C 5.09221 1.26979 0.11409
C 2.61301 -0.75044 -0.06778
C 3.72503 1.59851 0.14400
C 2.61299 0.75040 0.06780
H 6.78533 0.00005 -0.00002
H 5.78685 -2.11467 -0.18996
H 3.49270 -2.66832 -0.24051
H 5.78679 2.11474 0.18995
H 3.49262 2.66831 0.24054
C 1.25988 -1.14828 -0.10278
H 0.90882 -2.17834 -0.19429
C 0.42463 -0.00004 0.00000
C 1.25984 1.14821 0.10278
H 0.90876 2.17826 0.19429
B -1.12826 -0.00004 -0.00000
O -1.88904 1.14928 0.15263
O -1.88908 -1.14932 -0.15263
C -3.27953 0.78078 -0.13201
C -3.27957 -0.78076 0.13200
C -4.19345 -1.59594 -0.78806
H -4.09663 -2.66830 -0.55153
H -5.24980 -1.31013 -0.64476
H -3.93202 -1.45692 -1.84762
C -3.53705 1.14832 -1.60439
H -4.58749 0.97294 -1.89122
H -3.31152 2.21703 -1.75075
H -2.88697 0.56788 -2.27945
C -3.53712 -1.14829 1.60438
H -4.58756 -0.97291 1.89119
H -3.31159 -2.21700 1.75074
H -2.88705 -0.56785 2.27946
C -4.19338 1.59600 0.78805
H -4.09649 2.66836 0.55154
H -5.24974 1.31026 0.64474
H -3.93196 1.45695 1.84762

A-4
SCF (BP86) Energy = -796.510055957
Enthalpy 0K = -796.200926
Enthalpy 298K = -796.182172
Free Energy 298K = -796.246177
Lowest Frequency = 14.2830 cm^{-1}
Second Frequency = 45.9011 cm^{-1}
SCF (THF) Energy = -796.515434361
SCF (BP86-D3BJ) Energy = -796.584032750
SCF (BS2) Energy = -796.706586691

C 2.52417 -2.53667 -0.10596
C 3.82514 -2.00990 -0.08171
C 4.20620 -0.65866 -0.02163
C 1.28100 -1.88064 -0.07648

C	3.39832	0.48121	0.02645
C	0.95535	-0.50012	-0.01870
C	1.88174	0.57080	0.02645
H	4.64280	-2.73998	-0.11286
H	5.28800	-0.46442	-0.01118
H	0.41376	-2.55031	-0.10336
C	3.88709	1.80579	0.08386
H	4.94298	2.08327	0.09777
B	-0.60101	-0.22603	-0.01126
O	-1.50843	-1.26635	-0.15313
O	-1.21810	1.00536	0.13554
C	-2.84103	-0.72920	0.13814
C	-2.64813	0.81523	-0.14191
C	-3.44390	1.74837	0.77492
H	-3.21625	2.79764	0.52546
H	-4.52855	1.59530	0.64091
H	-3.19420	1.58866	1.83430
C	-3.13040	-1.04909	1.61539
H	-4.14823	-0.73992	1.90613
H	-3.04126	-2.13640	1.77070
H	-2.40799	-0.54928	2.28131
C	-2.86301	1.19887	-1.61631
H	-3.92862	1.15149	-1.89627
H	-2.50929	2.23042	-1.77428
H	-2.29344	0.53689	-2.28891
C	-3.85428	-1.43341	-0.76902
H	-3.89077	-2.50691	-0.52139
H	-4.86561	-1.01655	-0.62319
H	-3.58434	-1.33837	-1.83122
H	2.46541	-3.63231	-0.15376
C	2.78514	2.68622	0.11707
H	2.85242	3.77677	0.16276
C	1.57804	1.95215	0.08201
H	0.57183	2.36640	0.09872

A-5

SCF (BP86) Energy = -796.516035870
Enthalpy 0K = -796.206914
Enthalpy 298K = -796.188158
Free Energy 298K = -796.251893
Lowest Frequency = 27.2830 cm^{-1}
Second Frequency = 42.9252 cm^{-1}
SCF (THF) Energy = -796.521122495
SCF (BP86-D3BJ) Energy = -796.588542413
SCF (BS2) Energy = -796.713039424

C	-1.03066	1.80907	-0.10913
C	-2.31322	2.37954	-0.14534
C	-3.56777	1.74185	-0.10401
C	-0.61579	0.45513	-0.02815
C	-3.85253	0.37571	-0.01710
C	-2.86403	-0.75408	0.05121
H	-2.34205	3.47395	-0.21302
H	-4.44353	2.40490	-0.14432
C	-5.14101	-0.20794	0.02226
H	-6.08247	0.34410	-0.01050
B	0.92237	0.18523	-0.01395
O	1.87409	1.18626	-0.14034
O	1.47208	-1.08036	0.12655
C	3.17573	0.57820	0.15544
C	2.90879	-0.95471	-0.14126
C	3.65703	-1.93275	0.76923
H	3.38040	-2.96764	0.50915
H	4.74836	-1.83031	0.64093
H	3.41066	-1.77125	1.82919
C	3.47017	0.86777	1.63799
H	4.46949	0.50638	1.93296
H	3.43273	1.95650	1.80442
H	2.71917	0.39683	2.29331
C	3.11594	-1.33232	-1.61869
H	4.18426	-1.33414	-1.89247
H	2.71285	-2.34358	-1.78977
H	2.58358	-0.63580	-2.28703
C	4.23104	1.23842	-0.73675
H	4.32015	2.30637	-0.47837
H	5.21880	0.76927	-0.58778
H	3.96496	1.16744	-1.80186
H	-0.20527	2.53208	-0.15074
C	-4.99519	-1.61098	0.10983
H	-5.81970	-2.32718	0.15678
C	-3.62353	-1.94759	0.12736
H	-3.20437	-2.95378	0.18949
C	-1.46822	-0.67596	0.04106
H	-0.94967	-1.64364	0.09595

A-6

SCF (BP86) Energy = -796.513959141
Enthalpy 0K = -796.204880
Enthalpy 298K = -796.186114
Free Energy 298K = -796.249940
Lowest Frequency = 29.2059 cm^{-1}
Second Frequency = 36.8004 cm^{-1}
SCF (THF) Energy = -796.519178492
SCF (BP86-D3BJ) Energy = -796.586371730
SCF (BS2) Energy = -796.710910655

C	-0.53005	-0.00005	0.00006
C	-1.15912	1.26477	-0.10852
C	-2.52528	1.59265	-0.14027
C	-3.64190	0.75070	-0.06680
C	-3.64194	-0.75071	0.06681
H	-0.47238	2.11698	-0.17878
H	-2.75417	2.66381	-0.23448
C	-4.99585	1.15338	-0.10272
H	-5.34409	2.18392	-0.19421
B	1.03949	-0.00004	0.00002
O	1.79906	1.14643	-0.16242
O	1.79904	-1.14650	0.16247
C	3.19126	0.78166	0.12716
C	3.19136	-0.78162	-0.12715
C	4.10475	-1.59089	0.79789
H	4.00844	-2.66463	0.56793
H	5.16078	-1.30561	0.65202
H	3.84402	-1.44513	1.85667
C	3.44581	1.15915	1.59705
H	4.49599	0.98610	1.88567
H	3.22035	2.22878	1.73619
H	2.79582	0.58286	2.27574
C	3.44572	-1.15901	-1.59707
H	4.49593	-0.98609	-1.88570
H	3.22009	-2.22859	-1.73633
H	2.79584	-0.58252	-2.27568
C	4.10465	1.59083	-0.79801
H	4.00837	2.66460	-0.56815
H	5.16067	1.30553	-0.65218
H	3.84382	1.44497	-1.85676
C	-5.80732	0.00005	-0.00007
H	-6.90072	0.00007	-0.00011
C	-4.99591	-1.15332	0.10265
H	-5.34422	-2.18383	0.19413
C	-2.52535	-1.59268	0.14034
H	-2.75426	-2.66382	0.23455

C -1.15917 -1.26484 0.10866
H -0.47248 -2.11706 0.17891

B-1
SCF (BP86) Energy = -896.431843828
Enthalpy 0K = -896.123119
Enthalpy 298K = -896.103051
Free Energy 298K = -896.169631
Lowest Frequency = 20.6206 cm^{-1}
Second Frequency = 35.3899 cm^{-1}
SCF (THF) Energy = -896.496896649
SCF (BP86-D3BJ) Energy =
-896.509157771
SCF (BS2) Energy = -896.680722567

C   4.31539 1.74194 0.09212
C   4.88873 0.52584 -0.32392
C   4.25792 -0.72319 -0.50136
C   2.98460 2.03680 0.43829
C   2.92018 -1.07180 -0.29950
C   1.86229 1.18020 0.47405
C   1.78365 -0.18467 0.17762
H   5.96462 0.55346 -0.54310
H   4.91123 -1.54061 -0.84465
H   2.79105 3.08050 0.72044
H   0.89706 1.62544 0.75345
C   2.34765 -2.34693 -0.49921
H   2.89017 -3.22984 -0.85186
C   0.59388 -0.96597 0.25245
B -0.89718 -0.54674 0.77165
O -1.21975 0.91222 0.60873
O -1.92302 -1.25570 -0.05141
C -2.26547 1.04581 -0.34521
C -3.00355 -0.35388 -0.25115
C -3.76689 -0.76827 -1.52212
H -4.23173 -1.75896 -1.36946
H -4.57115 -0.04993 -1.76978
H -3.08538 -0.84742 -2.38389
C -1.64563 1.27062 -1.74711
H -2.40359 1.47958 -2.52597
H -0.95523 2.13025 -1.69539
H -1.06302 0.38300 -2.04234
C -3.96163 -0.42048 0.96645
H -4.86614 0.20465 0.83780
H -4.28005 -1.46903 1.10121
H -3.42606 -0.11278 1.87807
C -3.13135 2.26140 0.03349
H -2.53114 3.18598 -0.04453
H -4.00589 2.36685 -0.63620
H -3.48794 2.17934 1.07228
H   5.01398 2.58989 0.15036
C   0.97286 -2.27144 -0.17129
H   0.26903 -3.10760 -0.23738
F -1.01307 -0.87968 2.16362

B-2
SCF (BP86) Energy = -896.432439428
Enthalpy 0K = -896.123918
Enthalpy 298K = -896.103771
Free Energy 298K = -896.171140
Lowest Frequency = 16.9793 cm-1
Second Frequency = 30.3958 cm^{-1}
SCF (THF) Energy = -896.497760932
SCF (BP86-D3BJ) Energy =
-896.507900044
SCF (BS2) Energy = -896.682607514

C   5.55838 0.45142 0.28320
C   4.79510 1.57336 -0.08705
C   3.40999 1.65565 -0.34218
C   5.15015 -0.87947 0.49648
C   2.43972 0.64956 -0.29265
C   3.85907 -1.43434 0.39421
C   2.65126 -0.81226 0.05495
H   5.35336 2.51355 -0.19185
H   3.03478 2.65185 -0.62045
H   5.94686 -1.57987 0.78152
H   3.78402 -2.51070 0.61012
C   1.06272 0.78421 -0.56318
H   0.56403 1.71304 -0.85328
C   0.39008 -0.46479 -0.42024
C   1.38417 -1.41819 -0.04163
H   1.19049 -2.47917 0.14168
B -1.20512 -0.73376 -0.61478
O -1.86893 -1.06307 0.68865
O -1.87936 0.50913 -1.08717
C -2.80571 -0.03991 0.99764
C -3.13411 0.58635 -0.42116
C -3.58963 2.05609 -0.38976
H -3.77445 2.41037 -1.41984
H -4.52547 2.18201 0.18665
H -2.81331 2.70065 0.05233
C -2.12937 0.98710 1.94032
H -2.82760 1.76214 2.30999
H -1.71658 0.44577 2.80907
H -1.29171 1.47819 1.41884
C -4.17701 -0.25640 -1.19995
H -5.19607 -0.18139 -0.77450
H -4.20770 0.10557 -2.24253
H -3.86325 -1.31179 -1.22104
C -4.01112 -0.67350 1.71843
H -3.68556 -1.09783 2.68525
H -4.80463 0.07029 1.92287
H -4.43901 -1.49279 1.11964
F -1.38559 -1.83444 -1.51598
H   6.63186 0.64102 0.42683

B-4
SCF (BP86) Energy = -896.432761228
Enthalpy 0K = -896.124047
Enthalpy 298K = -896.104020
Free Energy 298K = -896.170400
Lowest Frequency = 18.7330 cm^{-1}
Second Frequency = 38.6447 cm^{-1}
SCF (THF) Energy = -896.496877186
SCF (BP86-D3BJ) Energy =
-896.510783132
SCF (BS2) Energy = -896.680888207

C   2.32230 -2.54720 -0.11672
C   3.62961 -2.12279 0.20222
C   4.08348 -0.80708 0.36185
C   1.15663 -1.80429 -0.35460
C   3.36112 0.38960 0.24555
C   0.91158 -0.40223 -0.36349
C   1.89935 0.57278 -0.09231
H   4.37760 -2.91545 0.34136
H   5.14971 -0.68992 0.61247
H   0.25887 -2.39776 -0.57255
C   3.90970 1.68270 0.42486
H   4.95358 1.89148 0.67702
B -0.62587 0.05805 -0.77976
O -1.59381 -1.08166 -0.74305
O -1.17337 1.05037 0.18930

C	-2.59616	-0.80990	0.22871
C	-2.56144	0.77010	0.33957
C	-3.03691	1.33620	1.68910
H	-2.96031	2.43812	1.67721
H	-4.09098	1.07053	1.89452
H	-2.41034	0.96638	2.51589
C	-2.19886	-1.48624	1.56446
H	-2.98037	-1.39633	2.34261
H	-2.01831	-2.55914	1.37744
H	-1.26377	-1.04361	1.94436
C	-3.34999	1.45009	-0.80877
H	-4.44534	1.32848	-0.70718
H	-3.11800	2.52937	-0.79848
H	-3.02131	1.04597	-1.77883
C	-3.93410	-1.39402	-0.26103
H	-3.85894	-2.49457	-0.32443
H	-4.76530	-1.14888	0.42690
H	-4.18174	-1.01639	-1.26538
H	2.19957	-3.63920	-0.19022
C	2.88265	2.63374	0.22260
H	3.00735	3.71946	0.29778
C	1.67445	1.97437	-0.08852
H	0.70095	2.42763	-0.27383
F	-0.57628	0.58100	-2.11430

B-5

SCF (BP86) Energy = -896.435314471
Enthalpy 0K = -896.126755
Enthalpy 298K = -896.106625
Free Energy 298K = -896.173919
Lowest Frequency = 12.3495 cm^{-1}
Second Frequency = 34.9332 cm^{-1}
SCF (THF) Energy = -896.498053150
SCF (BP86-D3BJ) Energy = -896.511773289
SCF (BS2) Energy = -896.684692636

C	-0.96207	1.75199	-0.35453
C	-2.20767	2.35135	-0.06274
C	-3.45009	1.74736	0.17638
C	-0.57915	0.40161	-0.50125
C	-3.76947	0.37995	0.19959
C	-2.82516	-0.76020	-0.03218
H	-2.20395	3.45014	-0.01580
H	-4.28951	2.43072	0.37899
C	-5.04255	-0.18398	0.45795
H	-5.95228	0.38426	0.66924
B	0.98430	0.08454	-0.90546
O	1.92484	1.15588	-0.45760
O	1.44278	-1.15308	-0.21170
C	2.79383	0.61538	0.52969
C	2.78947	-0.93422	0.19292
C	3.10738	-1.85624	1.38322
H	3.06422	-2.91123	1.05819
H	4.11921	-1.66629	1.78802
H	2.37202	-1.72490	2.19267
C	2.20010	0.89709	1.93258
H	2.87497	0.59593	2.75612
H	2.00521	1.97996	2.02124
H	1.24022	0.36748	2.04567
C	3.73731	-1.27219	-0.98617
H	4.80712	-1.19446	-0.71347
H	3.53518	-2.30827	-1.30924
H	3.52474	-0.60734	-1.83789
C	4.16836	1.29915	0.40954
H	4.07127	2.37445	0.64454
H	4.90629	0.86337	1.10934
H	4.55920	1.21402	-0.61655
H	-0.12734	2.45678	-0.48043
C	-4.92448	-1.59416	0.39822
H	-5.74633	-2.30078	0.55605
C	-3.59151	-1.95006	0.10502
H	-3.19548	-2.96194	-0.00696
C	-1.45525	-0.69939	-0.33380
H	-0.96984	-1.68049	-0.45022
F	1.06759	-0.04078	-2.33269

B-6

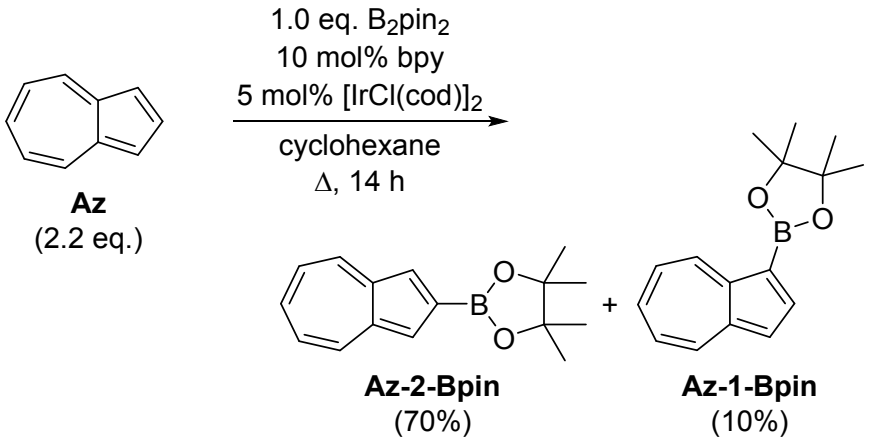
SCF (BP86) Energy = -896.437552147
Enthalpy 0K = -896.128886
Enthalpy 298K = -896.108758
Free Energy 298K = -896.176414
Lowest Frequency = 9.7828 cm^{-1}
Second Frequency = 30.0458 cm^{-1}
SCF (THF) Energy = -896.499628879
SCF (BP86-D3BJ) Energy = -896.513879613
SCF (BS2) Energy = -896.686617593

C	-0.48447	-0.08833	-0.52256
C	-1.13525	1.16925	-0.60118
C	-2.47798	1.52279	-0.39948
C	-3.57866	0.72211	-0.04575
C	-3.56322	-0.74572	0.21647
H	-0.46298	2.00040	-0.85333
H	-2.71405	2.59056	-0.53773
C	-4.91642	1.15778	0.13767
H	-5.26366	2.18759	0.02072
B	1.11813	-0.13177	-0.90064
O	1.82669	1.13198	-0.54162
O	1.79804	-1.19917	-0.11548
C	2.76379	0.85081	0.49065
C	3.06794	-0.69049	0.27855
C	3.53369	-1.43868	1.53982
H	3.70270	-2.50366	1.29948
H	4.48086	-1.02467	1.93352
H	2.77047	-1.39094	2.33254
C	2.09706	1.12000	1.86274
H	2.80085	1.02409	2.71111
H	1.69122	2.14630	1.86115
H	1.25745	0.42239	2.01491
C	4.08697	-0.92655	-0.86515
H	5.11562	-0.62248	-0.59295
H	4.09519	-2.00342	-1.10782
H	3.76900	-0.38092	-1.76732
C	3.98092	1.77887	0.32283
H	3.67173	2.82900	0.47209
H	4.77527	1.55032	1.05820
H	4.40130	1.69395	-0.69149
C	-5.70413	0.03874	0.49320
H	-6.77952	0.06412	0.69862
C	-4.89243	-1.11798	0.54425
H	-5.21832	-2.13146	0.79206
C	-2.44556	-1.59733	0.15633
H	-2.65998	-2.65161	0.39613
C	-1.10996	-1.30966	-0.16326
H	-0.42409	-2.16630	-0.12232
F	1.22986	-0.34561	-2.31427

Synthesis of Sensors

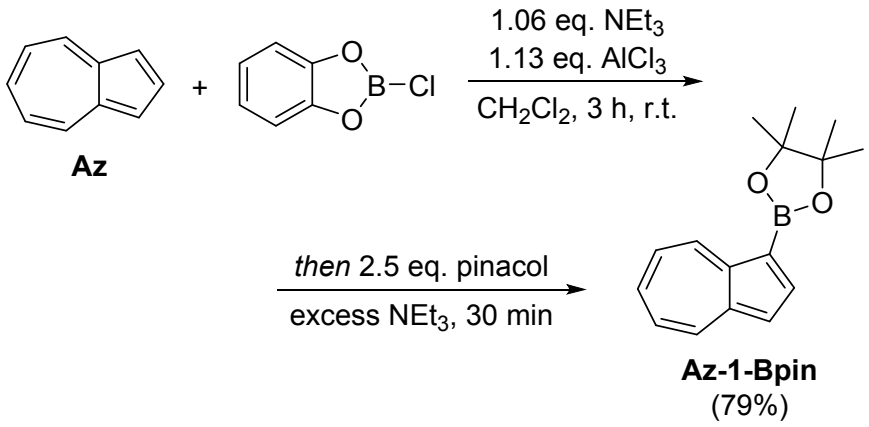
Scheme S1 – Synthetic routes to **Az-1-Bpin** and **Az-2-Bpin**.[6,7]

a) Murafuji-Sugihara synthesis:



Az-2-Bpin (70%) + **Az-1-Bpin** (10%)

b) Ingleson-Marcelli synthesis:



Az-1-Bpin (79%)

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Sample Preparation

Evaluation of selectivity in THF. A 1 mM solution of **Az-1-BPin** in THF was prepared and distributed to 5 one-millilitre vials, 0.1 mL per vial. 2 mM solutions of the tetra-*n*-butylammonium salts (fluoride, chloride, bromide, iodide) in THF were prepared and distributed in the vials, 0.9 ml per vial. The same procedure was repeated for **Az-2-BPin**.

Titration in THF. 16.5 mg (0.064 mmol) of **Az-2-BPin** were dissolved in 13 mL of THF to obtain a 5 mM solution. This solution was diluted to a concentration of 25 μM by adding 1 mL to 199 mL of THF. The absorbance spectrum of this solution was measured. After this, 0.1 equivalent of TBAF (1 μL of 0.5 M solution in THF) was added and the absorbance was measured. This process was repeated until 1.0 equivalents had been added, then additional TBAF was added in increments of 0.2 equivalents, until 2.0 equivalents of TBAF had been added.

Evaluation of selectivity in water. A solution of CTAB in water 92 mM was prepared, **Az-1-BPin** was diluted in it to obtain a 5 mM solution. The final solution was distributed in 9 vials, 0.4 ml per vial. A solution of TBAS 0.1 M in water was prepared and distributed in the 9 vials, 0.2 ml per vial. 5 mM solutions of the sodium salts in water were prepared and distributed in the vials, 0.4 ml per vial.

Tests in tap (faucet) and spring water. A solution of CTAB in water 92 mM was prepared and **Az-1-BPin** was diluted in it to obtain a 5 mM solution. The final solution was distributed to 5 vials, 0.2 ml per vial. A solution of TBAS 0.1 m in water was prepared and distributed in the 5 vials, 0.2 ml per vial. 0.6 ml of deionized water, tap water and spring water distributed in the 5 vials. 0.01 ml of a 1 M NaF were diluted in two vials.

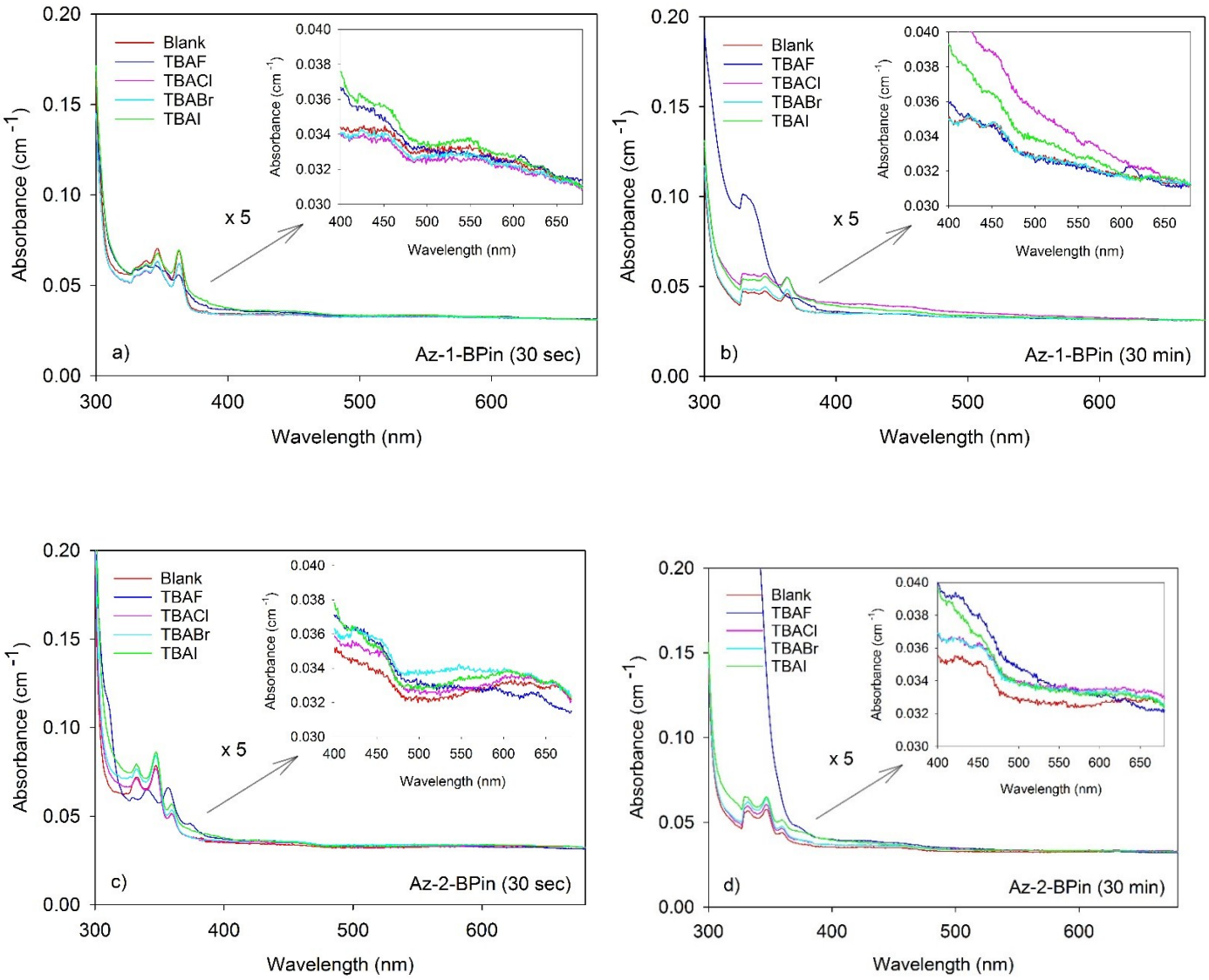

Figure S1: UV-vis absorption spectra for **Az-1-Bpin** (a-b) and **Az-2-Bpin** (c-d) upon exposure to tetra-*n*-butylammonium halides in THF. In each solution, [analyte] = 180 μM, which for TBAF corresponds to 3.4 mg/L of fluoride anion.

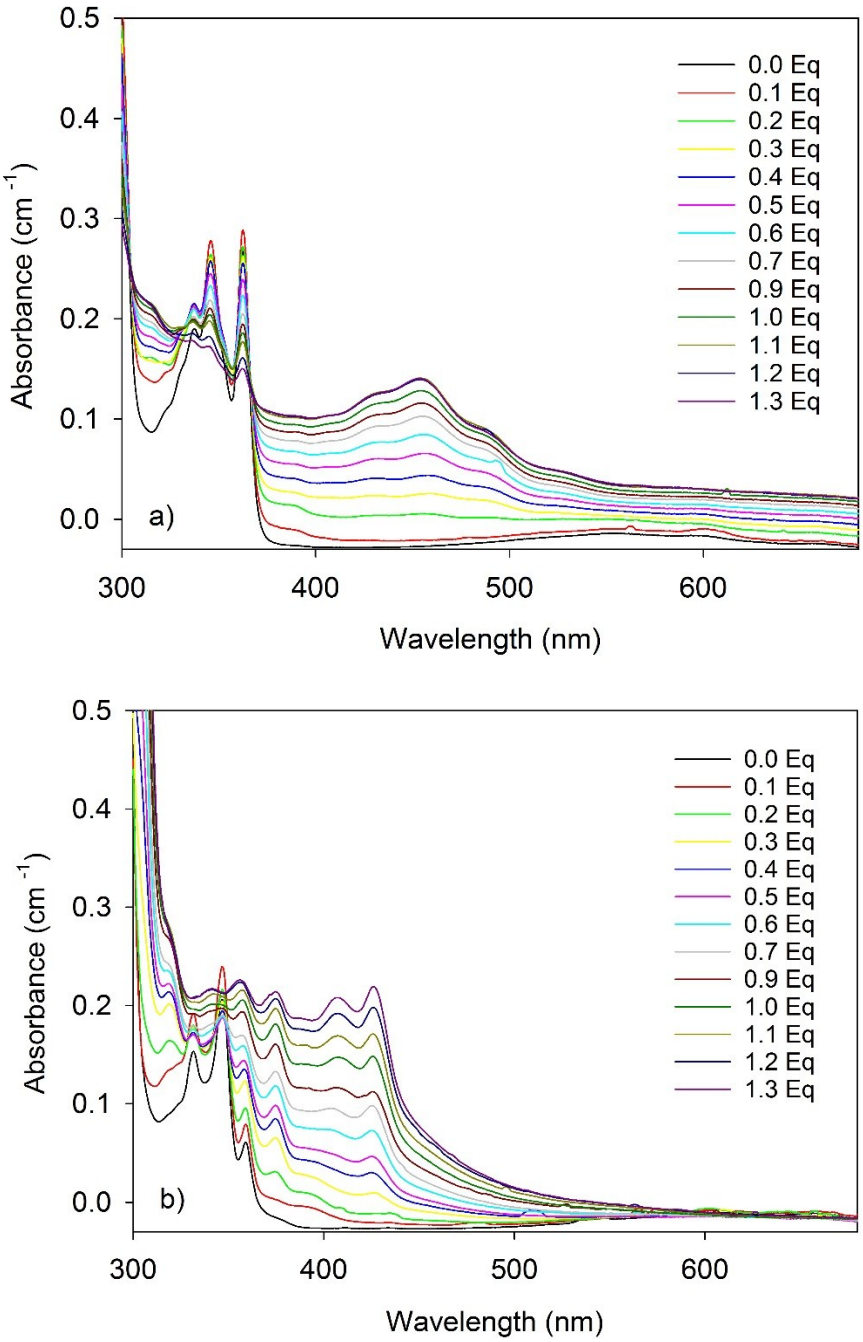

Figure S2: Absorption spectra for (*a*) **Az-1-BPin** and (*b*) **Az-2-Bpin** in THF, in the presence of different equivalents of TBAF after 30 min.

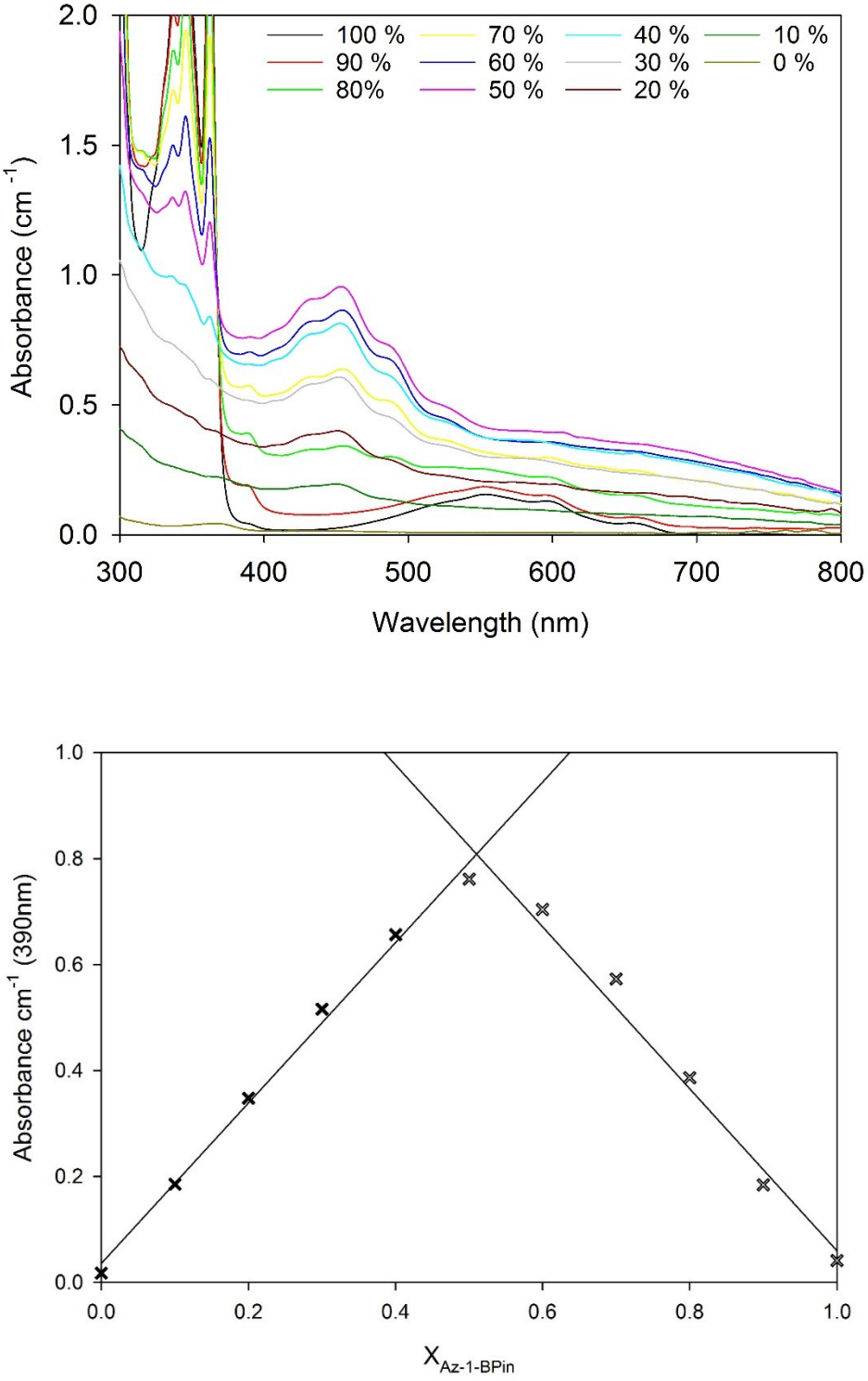

Figure S3: Job's plot (λ = 390 nm) for **Az-1-Bpin** with TBAF in THF.

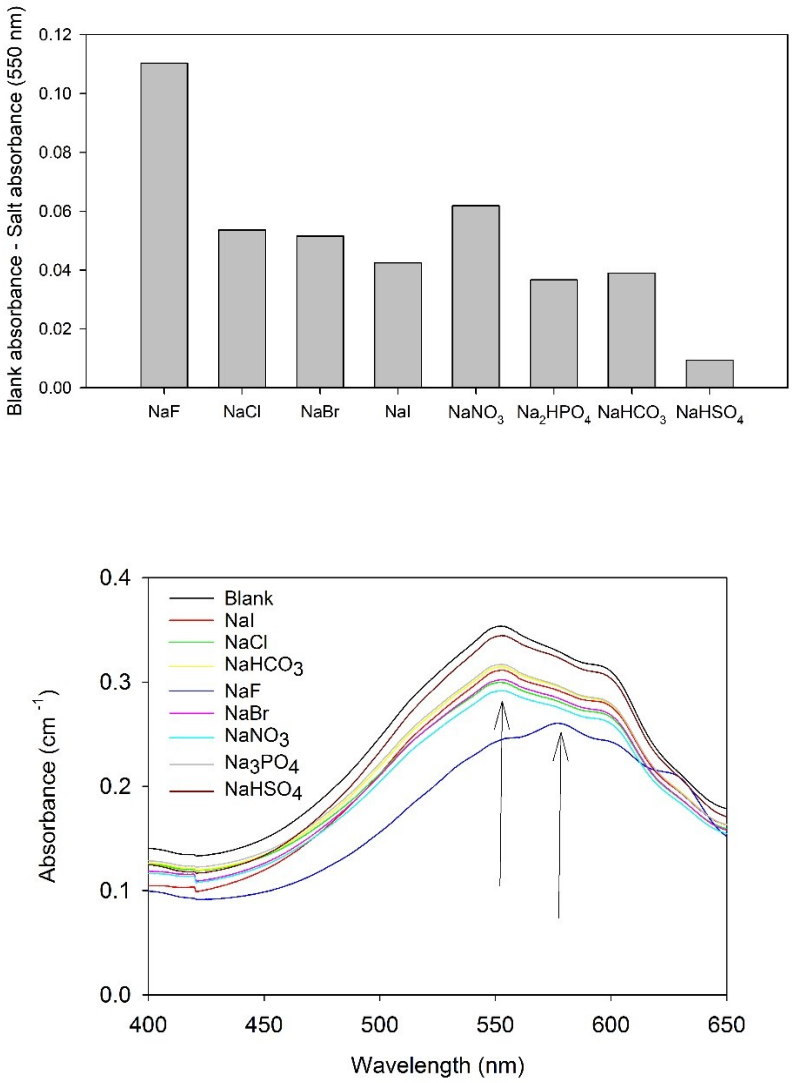

Figure S4. UV-Vis spectra for the selectivity test for **Az-1-BPin** in an aqueous micellar system. Spectra were acquired 30 mins after mixing all components.

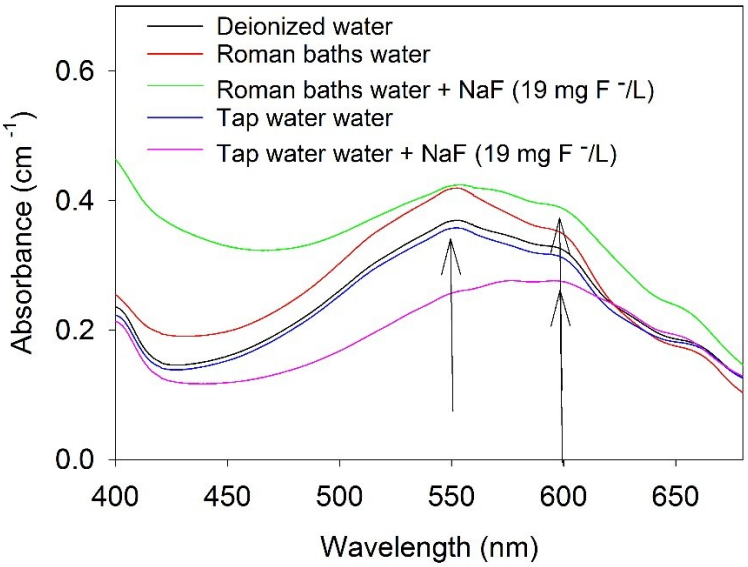

Figure S5. 1. Deionized water 2. Bath tap water 3. Bath tap water + NaF 4. Roman Baths spring water 5. Roman Baths spring water + NaF. Spectra and photographs were acquired 30 mins after mixing all components.

Tap (faucet) water from the public water supply in the city of Bath (England) was evaluated, as was spring water from the Roman Baths for which the city was named. Samples of the above to which sodium fluoride was deliberately added were evaluated for comparison. It can be seen that the absorption spectra for the tap water and deionized water are essentially equivalent. Samples containing spring water from the Roman Baths showed higher absorbance due to higher turbidity, but the visible region λ_{max} for all three samples lacking fluoride was the same (550 nm). In contrast, both samples to which fluoride was added exhibited altered absorption spectra and the same colour change visible to the naked eye.

Titration and Limit Of Detection (LOD) for Az-1-BPin for aqueous micellar system

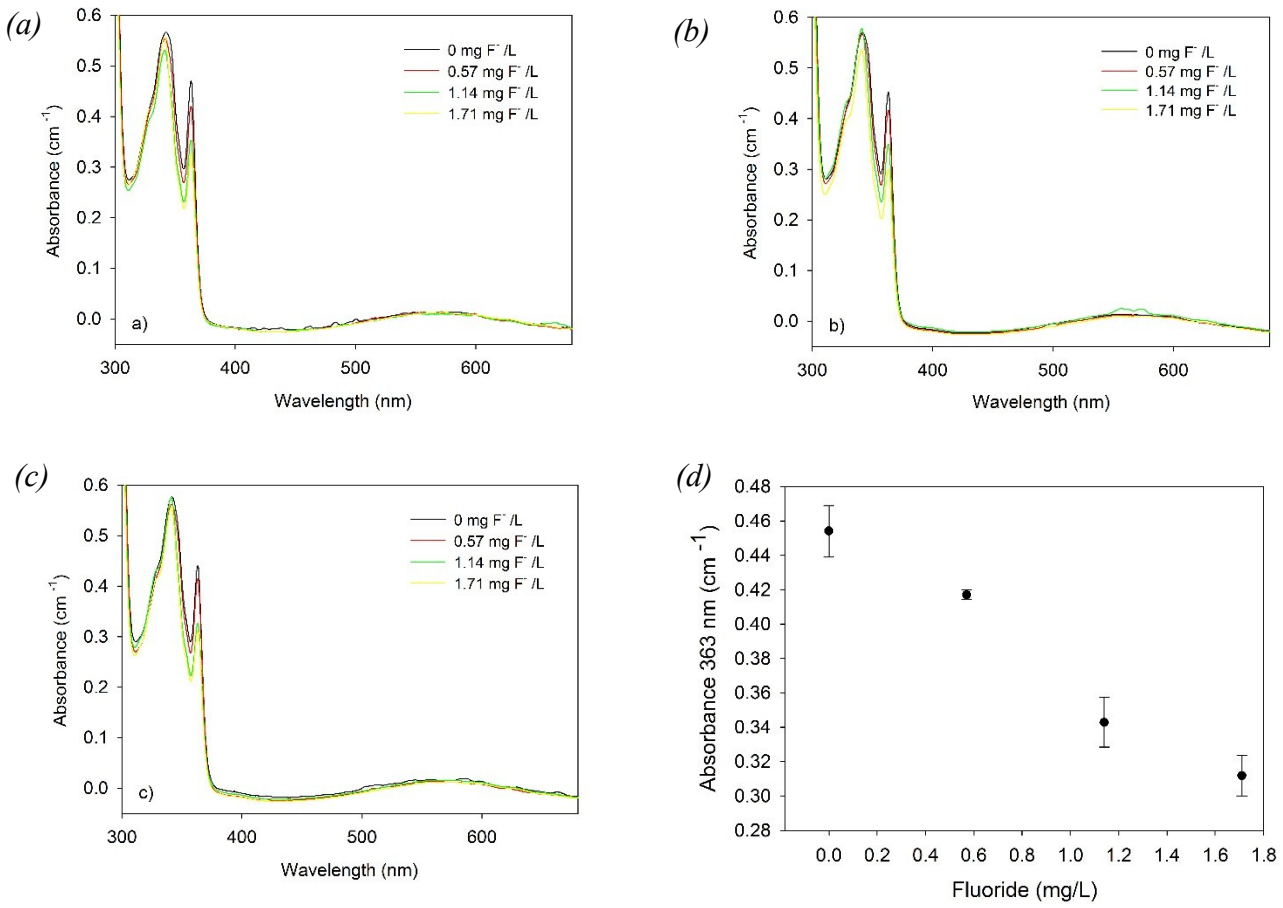

Figure S6. Titrations of **Az-1-Bpin** in the aqueous micellar system; four different fluoride concentrations used. (*a-c*) Data acquired in triplicate. (*d*) Dose-response plot at 363 nm implies a Limit of Detection at this wavelength of ≈ 0.2-0.4 mg/L, i.e. below the WHO recommended threshold of 1.5 mg/L.

Each sample contained 30 µL of a 5mM solution of **Az-1-Bpin** in CTAB/deionised water (0.01M), and 0.2 mL TBAS (0.1 M). NaF in water (5mM) was added to achieve the desired fluoride concentration (0, 0.57, 1.14 or 1.71 mg/L fluoride). The total sample volume was made up to 1 mL with additional deionised water. Spectra were acquired 30 mins after mixing.

Small-Angle X-Ray Scattering.

Small-angle X-Ray scattering (SAXS) experiments were performed in a slit-collimated Anton Paar SAXSess with a PANalytical PW3830 generator, with a Cu Kα source (λ = 1.5406Å) operated at 40 kV and 5o mA Data were collected using an image plate detector, read on a Perkins Elmer Cyclone Storage Phosphor System. Samples were loaded in 1.5 mm borosilicate glass capillaries. Samples were placed in a temperature controlled sample holder at 30 ˚C and exposed to the X-ray beam for 180 minutes. Data were subsequently reduced and background scattering subtracted using Anton Paar SAXSQuant software. SAXS data were subsequently analysed using SasView 4.1.[8]

A sample containing a mixture of CTAB and TBAS (92 mM/0.1 M respectively) and a sample containing the sensor, CTAB and TBAS (5 mM/92 mM/0.1 mM respectively). The data were analysed using the Guinier approximation in order to follow changes in size of the aggregates with the addition of the sensor molecule. Further details regarding the aggregate morphology were obtained through model-based fitting using a charged uniform ellipsoid model.[9] The electrostatic interactions between micelles were accounted for using the Hayter-Penfold mean spherical approximation to describe the screened Coulomb repulsion between tumbling charged particles in solution.[10]

This research benefited from the use of the SasView application, originally developed under NSF Award DMR-0520547. SasView also contains code developed with funding from the EU Horizon 2020 programme under the SINE2020 project, #654000.

Single crystal X-ray structural analysis.

Data were collected at 150(2) K on a Rigaku SuperNova, Dual, Cu at zero, EosS2 single crystal diffractometer using a micro-focus sealed X-ray tube Cu-Kα radiation λ = 1.51484 Å. Unit cell determination, data collection and data reduction were performed using CrysAlisPro.[11] A symmetry-related (multi-scan) absorption correction had been applied. The structure was solved with SHELXT followed by full-matrix least squares refinement on F^2 using (Shelxl-2014).[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed onto calculated positions and refined using a riding model. The crystallographic data in CIF format for **Az-1-Bpin** has been deposited with **CCDC #1568176**. These data can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Table S1. Crystal data and structure refinement for **Az-1-Bpin**.

Empirical formula	$C_{16}H_{19}BO_2$	
Formula weight	254.12	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.4172(9) Å	α= 90°.
	b = 11.5094(9) Å	β= 99.589(13)°.
	c = 12.3947(19) Å	γ = 90°.
Volume	1465.3(3) $Å^3$	
Z	4	
Density (calculated)	1.152 Mg/m^3	
Absorption coefficient	0.573 mm^{-1}	
F(000)	544	
Crystal size	0.150 x 0.120 x 0.030 mm^3	
Theta range for data collection	5.143 to 68.416°.	
Index ranges	-7<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	8634	
Independent reflections	2686 [R(int) = 0.0521]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.91713	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2686 / 0 / 176	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0637, wR2 = 0.1583	
R indices (all data)	R1 = 0.1015, wR2 = 0.1844	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.204 and -0.220 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **Az-1-Bpin**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B	5642(3)	5883(3)	2970(3)	45(1)
O(1)	6461(2)	5177(2)	3650(2)	57(1)
O(2)	5482(2)	5547(2)	1908(2)	55(1)
C(1)	7119(3)	4446(2)	2951(3)	54(1)
C(2)	7446(3)	3293(2)	3516(3)	64(1)
C(3)	8367(3)	5072(3)	2813(4)	82(1)
C(4)	6123(3)	4412(3)	1889(3)	62(1)
C(5)	5075(4)	3496(3)	1912(4)	105(2)
C(6)	6722(5)	4340(4)	858(3)	100(2)
C(7)	5019(2)	6977(2)	3394(2)	44(1)
C(8)	5125(3)	7291(2)	4500(3)	52(1)
C(9)	4509(3)	8346(3)	4617(3)	54(1)
C(10)	3997(2)	8755(2)	3570(3)	48(1)
C(11)	3364(3)	9811(2)	3336(3)	55(1)
C(12)	2855(3)	10279(3)	2333(3)	62(1)
C(13)	2805(3)	9809(3)	1307(3)	62(1)
C(14)	3285(3)	8755(2)	1006(3)	56(1)
C(15)	3969(2)	7897(2)	1660(3)	50(1)
C(16)	4316(2)	7872(2)	2786(2)	42(1)

Table S3. Bond lengths [Å] for **Az-1-Bpin**.

B-O(2)	1.356(4)	C(6)-H(6B)	0.9800
B-O(1)	1.363(4)	C(6)-H(6C)	0.9800
B-C(7)	1.548(4)	C(7)-C(8)	1.404(4)
O(1)-C(1)	1.458(3)	C(7)-C(16)	1.408(4)
O(2)-C(4)	1.469(3)	C(8)-C(9)	1.392(4)
C(1)-C(2)	1.513(4)	C(8)-H(8)	0.9500
C(1)-C(3)	1.521(4)	C(9)-C(10)	1.400(4)
C(1)-C(4)	1.535(5)	C(9)-H(9)	0.9500
C(2)-H(2A)	0.9800	C(10)-C(11)	1.390(4)
C(2)-H(2B)	0.9800	C(10)-C(16)	1.482(4)
C(2)-H(2C)	0.9800	C(11)-C(12)	1.377(5)
C(3)-H(3A)	0.9800	C(11)-H(11)	0.9500
C(3)-H(3B)	0.9800	C(12)-C(13)	1.375(5)
C(3)-H(3C)	0.9800	C(12)-H(12)	0.9500
C(4)-C(6)	1.514(5)	C(13)-C(14)	1.386(4)
C(4)-C(5)	1.521(5)	C(13)-H(13)	0.9500
C(5)-H(5A)	0.9800	C(14)-C(15)	1.396(4)
C(5)-H(5B)	0.9800	C(14)-H(14)	0.9500
C(5)-H(5C)	0.9800	C(15)-C(16)	1.382(4)
C(6)-H(6A)	0.9800	C(15)-H(15)	0.9500

Table S4. Bond lengths [Å] and angles [°] for **Az-1-Bpin**.

O(2)-B-O(1)	113.1(2)	C(4)-C(6)-H(6B)	109.5
O(2)-B-C(7)	124.8(3)	H(6A)-C(6)-H(6B)	109.5
O(1)-B-C(7)	122.0(3)	C(4)-C(6)-H(6C)	109.5
B-O(1)-C(1)	106.5(2)	H(6A)-C(6)-H(6C)	109.5
B-O(2)-C(4)	106.7(2)	H(6B)-C(6)-H(6C)	109.5
O(1)-C(1)-C(2)	108.8(2)	C(8)-C(7)-C(16)	106.5(2)
O(1)-C(1)-C(3)	106.8(2)	C(8)-C(7)-B	124.9(3)
C(2)-C(1)-C(3)	109.7(3)	C(16)-C(7)-B	128.6(3)
O(1)-C(1)-C(4)	101.9(2)	C(9)-C(8)-C(7)	111.4(3)
C(2)-C(1)-C(4)	116.3(3)	C(9)-C(8)-H(8)	124.3
C(3)-C(1)-C(4)	112.6(3)	C(7)-C(8)-H(8)	124.3
C(1)-C(2)-H(2A)	109.5	C(8)-C(9)-C(10)	107.9(3)
C(1)-C(2)-H(2B)	109.5	C(8)-C(9)-H(9)	126.1
H(2A)-C(2)-H(2B)	109.5	C(10)-C(9)-H(9)	126.1
C(1)-C(2)-H(2C)	109.5	C(11)-C(10)-C(9)	125.6(3)
H(2A)-C(2)-H(2C)	109.5	C(11)-C(10)-C(16)	127.8(3)
H(2B)-C(2)-H(2C)	109.5	C(9)-C(10)-C(16)	106.6(2)
C(1)-C(3)-H(3A)	109.5	C(12)-C(11)-C(10)	128.9(3)
C(1)-C(3)-H(3B)	109.5	C(12)-C(11)-H(11)	115.5
H(3A)-C(3)-H(3B)	109.5	C(10)-C(11)-H(11)	115.5
C(1)-C(3)-H(3C)	109.5	C(13)-C(12)-C(11)	129.1(3)
H(3A)-C(3)-H(3C)	109.5	C(13)-C(12)-H(12)	115.4
H(3B)-C(3)-H(3C)	109.5	C(11)-C(12)-H(12)	115.4
O(2)-C(4)-C(6)	108.3(3)	C(12)-C(13)-C(14)	129.3(3)
O(2)-C(4)-C(5)	106.6(3)	C(12)-C(13)-H(13)	115.4
C(6)-C(4)-C(5)	112.1(3)	C(14)-C(13)-H(13)	115.4
O(2)-C(4)-C(1)	102.0(2)	C(13)-C(14)-C(15)	129.4(3)
C(6)-C(4)-C(1)	114.2(3)	C(13)-C(14)-H(14)	115.3
C(5)-C(4)-C(1)	112.7(3)	C(15)-C(14)-H(14)	115.3
C(4)-C(5)-H(5A)	109.5	C(16)-C(15)-C(14)	128.5(3)
C(4)-C(5)-H(5B)	109.5	C(16)-C(15)-H(15)	115.7
H(5A)-C(5)-H(5B)	109.5	C(14)-C(15)-H(15)	115.7
C(4)-C(5)-H(5C)	109.5	C(15)-C(16)-C(7)	125.5(2)
H(5A)-C(5)-H(5C)	109.5	C(15)-C(16)-C(10)	126.8(2)
H(5B)-C(5)-H(5C)	109.5	C(7)-C(16)-C(10)	107.7(2)
C(4)-C(6)-H(6A)	109.5		

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **Az-1-Bpin**. 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}
B	36(2)	36(2)	63(2)	6(1)	10(1)	0(1)
O(1)	59(1)	44(1)	68(2)	-1(1)	11(1)	18(1)
O(2)	58(1)	44(1)	63(1)	-2(1)	8(1)	18(1)
C(1)	51(2)	37(1)	75(2)	2(1)	18(2)	11(1)
C(2)	67(2)	40(2)	87(2)	9(2)	20(2)	16(1)
C(3)	48(2)	50(2)	152(4)	12(2)	31(2)	9(2)
C(4)	66(2)	45(2)	74(2)	-7(2)	10(2)	21(1)
C(5)	69(2)	50(2)	185(5)	-41(3)	-9(3)	9(2)
C(6)	127(4)	100(3)	77(3)	-2(2)	28(2)	61(3)
C(7)	34(1)	35(1)	62(2)	-1(1)	9(1)	-1(1)
C(8)	46(2)	45(2)	65(2)	3(1)	10(1)	6(1)
C(9)	53(2)	50(2)	63(2)	-8(1)	18(1)	-1(1)
C(10)	35(1)	38(1)	72(2)	-4(1)	16(1)	-1(1)
C(11)	42(2)	41(2)	85(2)	-6(2)	17(2)	1(1)
C(12)	42(2)	45(2)	97(3)	2(2)	11(2)	7(1)
C(13)	49(2)	49(2)	84(3)	10(2)	-1(2)	5(1)
C(14)	50(2)	44(2)	71(2)	1(2)	0(1)	3(1)
C(15)	40(1)	37(1)	73(2)	-1(1)	10(1)	-1(1)
C(16)	32(1)	30(1)	66(2)	-2(1)	12(1)	-4(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **Az-1-Bpin**.

	x	y	z	U(eq)
H(2A)	7885	2793	3051	95
H(2B)	6643	2916	3649	95
H(2C)	8022	3423	4216	95
H(3A)	8847	4604	2353	123
H(3B)	8906	5189	3532	123
H(3C)	8152	5828	2464	123
H(5A)	5441	2724	1825	157
H(5B)	4351	3640	1313	157
H(5C)	4759	3536	2612	157
H(6A)	7262	3641	883	150
H(6B)	7262	5029	806	150
H(6C)	6029	4305	219	150
H(8)	5561	6842	5092	63
H(9)	4446	8721	5289	65
H(11)	3270	10274	3952	66
H(12)	2487	11032	2353	74
H(13)	2381	10273	720	74
H(14)	3124	8593	244	67
H(15)	4230	7243	1281	60

Table S7. Torsion angles [°] for **Az-1-Bpin**.

O(2)-B-O(1)-C(1)	12.8(3)	O(1)-B-C(7)-C(16)	170.0(2)
C(7)-B-O(1)-C(1)	-165.0(2)	C(16)-C(7)-C(8)-C(9)	0.4(3)
O(1)-B-O(2)-C(4)	8.1(3)	B-C(7)-C(8)-C(9)	177.3(2)
C(7)-B-O(2)-C(4)	-174.2(3)	C(7)-C(8)-C(9)-C(10)	-0.9(3)
B-O(1)-C(1)-C(2)	-150.1(3)	C(8)-C(9)-C(10)-C(11)	-176.7(3)
B-O(1)-C(1)-C(3)	91.5(3)	C(8)-C(9)-C(10)-C(16)	0.9(3)
B-O(1)-C(1)-C(4)	-26.8(3)	C(9)-C(10)-C(11)-C(12)	178.9(3)
B-O(2)-C(4)-C(6)	-144.8(3)	C(16)-C(10)-C(11)-C(12)	1.8(5)
B-O(2)-C(4)-C(5)	94.4(3)	C(10)-C(11)-C(12)-C(13)	2.2(5)
B-O(2)-C(4)-C(1)	-24.0(3)	C(11)-C(12)-C(13)-C(14)	-2.0(6)
O(1)-C(1)-C(4)-O(2)	30.4(3)	C(12)-C(13)-C(14)-C(15)	-1.4(6)
C(2)-C(1)-C(4)-O(2)	148.6(3)	C(13)-C(14)-C(15)-C(16)	1.7(5)
C(3)-C(1)-C(4)-O(2)	-83.7(3)	C(14)-C(15)-C(16)-C(7)	-179.5(3)
O(1)-C(1)-C(4)-C(6)	147.0(3)	C(14)-C(15)-C(16)-C(10)	2.1(4)
C(2)-C(1)-C(4)-C(6)	-94.8(4)	C(8)-C(7)-C(16)-C(15)	-178.5(2)
C(3)-C(1)-C(4)-C(6)	32.9(4)	B-C(7)-C(16)-C(15)	4.7(4)
O(1)-C(1)-C(4)-C(5)	-83.6(3)	C(8)-C(7)-C(16)-C(10)	0.2(3)
C(2)-C(1)-C(4)-C(5)	34.6(4)	B-C(7)-C(16)-C(10)	-176.5(2)
C(3)-C(1)-C(4)-C(5)	162.4(3)	C(11)-C(10)-C(16)-C(15)	-4.5(4)
O(2)-B-C(7)-C(8)	176.3(3)	C(9)-C(10)-C(16)-C(15)	178.0(2)
O(1)-B-C(7)-C(8)	-6.2(4)	C(11)-C(10)-C(16)-C(7)	176.8(3)
O(2)-B-C(7)-C(16)	-7.6(4)	C(9)-C(10)-C(16)-C(7)	-0.7(3)

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