Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Sensing mechanism for fluoride chemosensor: Invalidity of excited-state proton transfer mechanism

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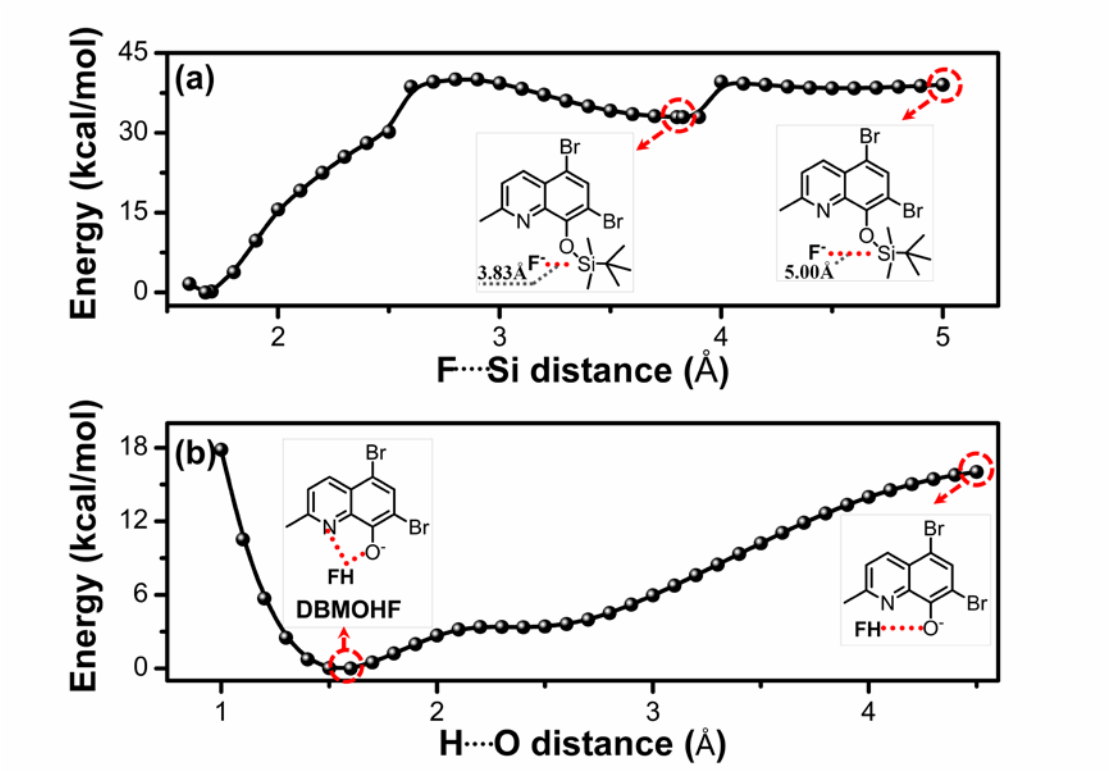

Figure S1 Potential-energy curves of ground state for (a) DBM with the addition of fluoride anion, which is the function of F···Si distance in ground state, (b) DBMO with the HF molecule, which is the function of FH···O distance in the ground state.

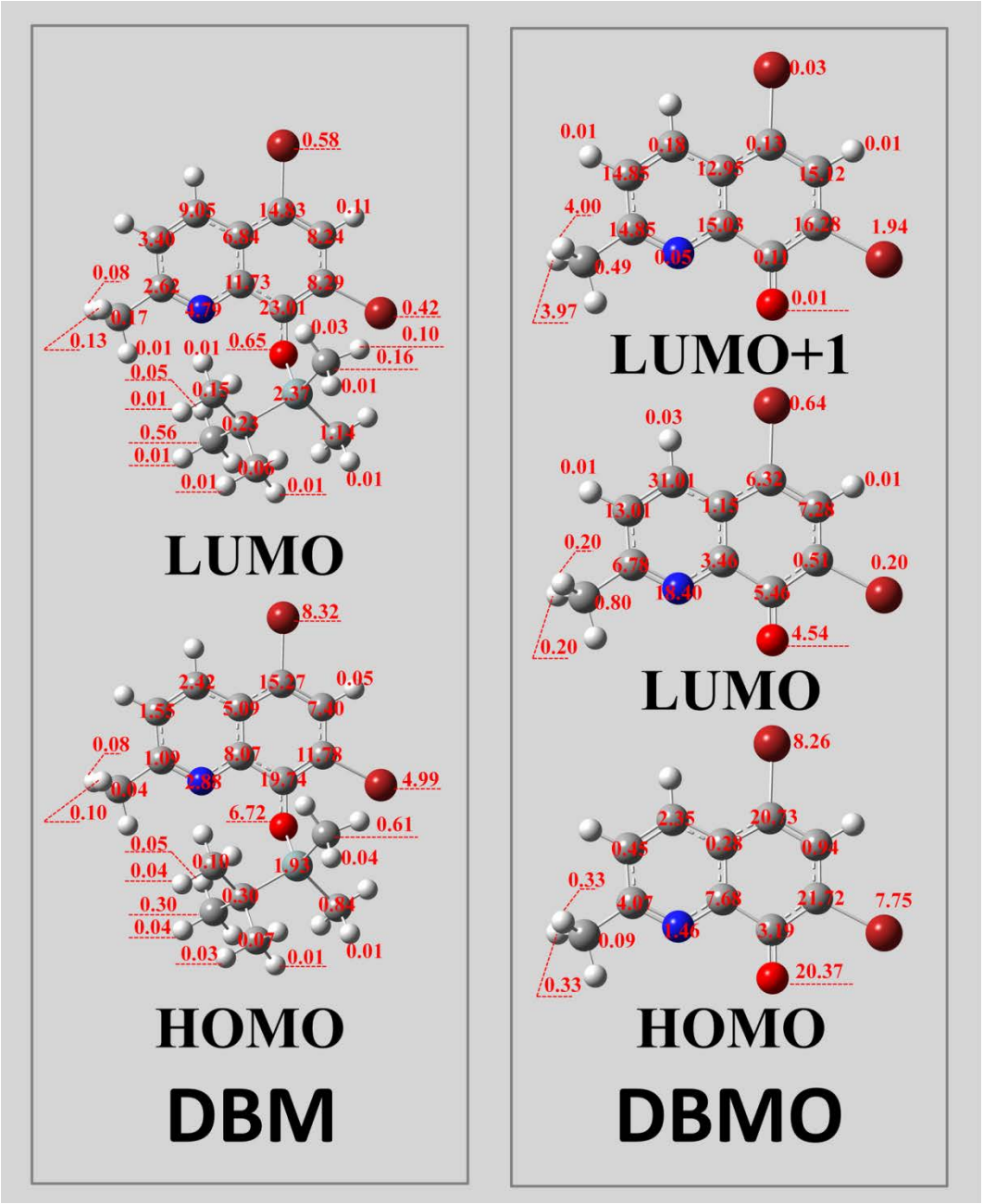

Figure S2. Contribution (%) of some atoms (contribution > 0.01%) to frontier molecular orbitals (HOMO and LUMO for DBM, HOMO, LUMO and LUMO+1 for DBMO). The contribution value was calculated by C-squared Population Analysis (SCPA) method.[2]

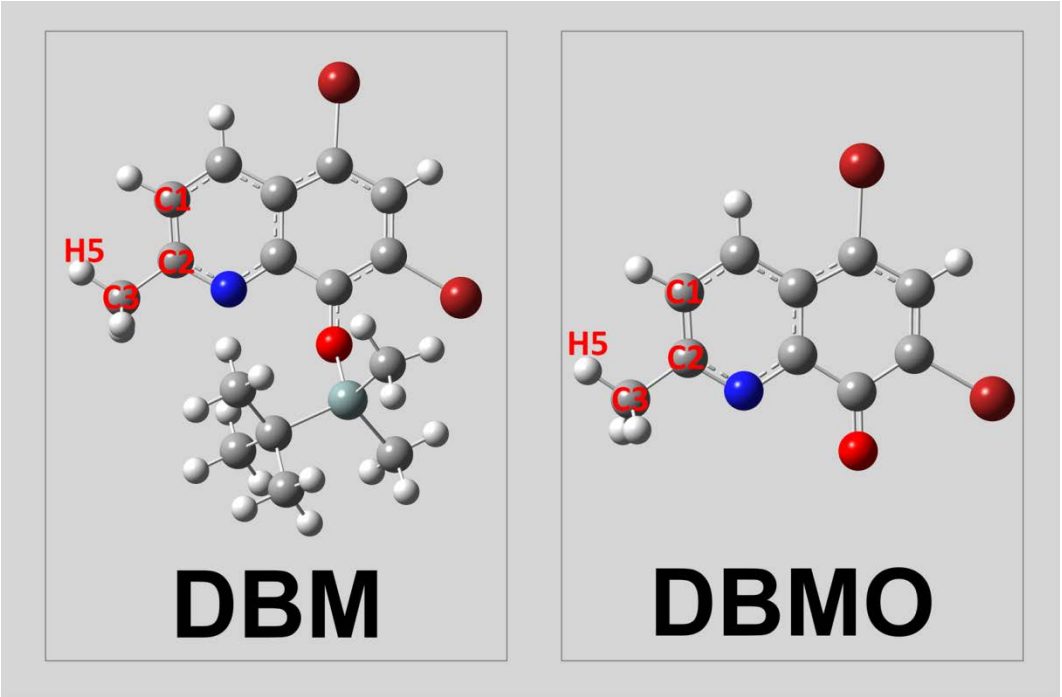

Figure S3. Views of the optimized S_1 structures for DBM and DBMO using B3LYP/TZVP, Gray: C; white: H; red: O; blue: N; dark cyan: Si; dark red: Br.

Cartesian coordinates of the optimized geometries for the ground state S_0 of DBM at B3LYP/TZVP level

C	1.768219000	3.472550000	-0.241063000
C	2.557787000	2.378236000	-0.035032000
C	1.993266000	1.081622000	-0.085505000
C	0.589155000	0.998219000	-0.340970000
C	0.384969000	3.298057000	-0.503285000
H	2.187628000	4.470096000	-0.211002000
H	3.615568000	2.489479000	0.160307000
C	2.722100000	-0.120358000	0.078542000
C	-0.065017000	-0.282971000	-0.400632000
C	0.729865000	-1.409284000	-0.270677000
C	2.112083000	-1.339503000	-0.017080000
H	2.678528000	-2.252605000	0.090178000
N	-0.171203000	2.104389000	-0.541939000
C	-0.488333000	4.497930000	-0.743392000
H	-0.525264000	5.133485000	0.145699000
H	-0.092103000	5.108777000	-1.558246000
H	-1.499693000	4.186359000	-0.993720000
O	-1.374995000	-0.348232000	-0.668386000
Si	-2.794988000	-0.622474000	0.267769000
C	-3.838477000	0.989618000	0.336492000

C	-3.722589000	-1.969069000	-0.667678000
H	-3.096034000	-2.854826000	-0.776845000
H	-4.631965000	-2.257344000	-0.136115000
H	-4.008302000	-1.631145000	-1.666108000
Br	4.614443000	-0.082085000	0.435483000
Br	-0.020452000	-3.161910000	-0.465185000
C	-2.271727000	-1.187089000	1.989954000
H	-1.565266000	-0.490442000	2.445557000
H	-3.143691000	-1.252490000	2.645080000
H	-1.804604000	-2.172281000	1.953975000
C	-3.209087000	2.009704000	1.303044000
H	-2.200727000	2.283486000	0.991164000
H	-3.814191000	2.923668000	1.325539000
H	-3.162698000	1.626215000	2.325416000
C	-5.253264000	0.635028000	0.839682000
H	-5.853565000	1.547610000	0.926832000
H	-5.778185000	-0.035868000	0.156302000
H	-5.237465000	0.164721000	1.827013000
C	-3.942424000	1.611844000	-1.067912000
H	-4.554820000	2.520387000	-1.030133000
H	-2.959106000	1.882715000	-1.453797000
H	-4.414686000	0.932398000	-1.782581000

Cartesian coordinates of the optimized geometries for the ground state S_0 of DBMF at B3LYP/TZVP level

C	0.440511000	-0.675381000	-0.691497000
C	1.784719000	-0.932033000	-0.710973000
C	2.715490000	0.122633000	-0.549207000
C	2.171481000	1.436879000	-0.370300000
C	-0.010992000	0.652495000	-0.508179000
H	-0.275794000	-1.479051000	-0.814894000
H	2.148542000	-1.941750000	-0.849951000
C	4.120464000	-0.034560000	-0.552854000
C	3.031029000	2.632885000	-0.190582000
C	4.421302000	2.322181000	-0.212646000
C	4.954122000	1.046861000	-0.386509000
H	6.027213000	0.913057000	-0.390051000
N	0.836128000	1.652881000	-0.356138000
C	-1.486096000	0.958693000	-0.479722000
H	-1.974400000	0.636955000	-1.403956000
H	-1.981375000	0.436276000	0.343986000
H	-1.642788000	2.029014000	-0.356337000
O	2.556678000	3.785783000	-0.037808000
Si	0.164751000	7.395739000	0.333046000
C	-0.212102000	9.274151000	0.406259000

C	0.858194000	6.714368000	1.941357000
H	1.040893000	5.643153000	1.834838000
H	1.810435000	7.188473000	2.190628000
H	0.171395000	6.869951000	2.775544000
Br	4.925547000	-1.783691000	-0.791105000
Br	5.665867000	3.786179000	0.016179000
C	1.205248000	6.897251000	-1.146709000
H	0.675056000	7.077799000	-2.084097000
H	2.141798000	7.459951000	-1.172976000
H	1.457843000	5.836225000	-1.078672000
C	-0.857097000	9.726458000	-0.917778000
H	-1.790715000	9.194727000	-1.116972000
H	-1.089465000	10.796907000	-0.877374000
H	-0.192793000	9.568072000	-1.770760000
C	1.096083000	10.057646000	0.627709000
H	0.888496000	11.133215000	0.667475000
H	1.583532000	9.786424000	1.567667000
H	1.814254000	9.895500000	-0.180100000
C	-1.182616000	9.567190000	1.566156000
H	-1.420877000	10.636619000	1.597377000
H	-2.123510000	9.023032000	1.454780000
H	-0.753649000	9.300396000	2.535110000

F	-1.317315000	6.662697000	0.128778000

Cartesian coordinates of the optimized geometries for the ground state S_0 of DBMO at B3LYP/TZVP level

C	-3.446529000	-0.823885000	0.001375000
C	-2.637075000	0.279779000	0.000074000
C	-1.228803000	0.132676000	-0.001329000
C	-0.723565000	-1.209036000	-0.002586000
C	-2.864077000	-2.112740000	0.001197000
H	-4.524813000	-0.716576000	0.002807000
H	-3.065153000	1.273737000	0.000426000
C	-0.305816000	1.203514000	-0.000699000
C	0.730161000	-1.510220000	-0.004852000
C	1.537148000	-0.334972000	-0.000940000
C	1.050125000	0.969888000	-0.000014000
H	1.744538000	1.798898000	0.001421000
N	-1.554686000	-2.277049000	-0.001337000
C	-3.734146000	-3.342760000	0.004918000
H	-4.376636000	-3.370142000	0.889771000
H	-4.390417000	-3.366358000	-0.869792000
H	-3.112660000	-4.236465000	-0.001545000
Br	-0.916841000	3.044787000	-0.000377000
Br	3.458539000	-0.573019000	0.002551000

O	1.172999000	-2.683637000	-0.009086000

Cartesian coordinates of the optimized geometries for the ground state S_0 of DBMOHF at B3LYP/TZVP level

C	2.247260000	2.683924000	0.000062000
C	2.376225000	1.322090000	0.000070000
C	1.225364000	0.497039000	0.000203000
C	-0.040138000	1.165795000	0.000389000
C	0.953954000	3.261907000	0.000224000
H	3.123802000	3.320475000	-0.000128000
H	3.356182000	0.863225000	-0.000128000
C	1.240561000	-0.916789000	0.000019000
C	-1.306864000	0.429043000	0.000391000
C	-1.159086000	-0.972879000	0.000227000
C	0.071291000	-1.635811000	0.000103000
H	0.093100000	-2.716511000	-0.000069000
N	-0.131944000	2.516106000	0.000442000
C	0.782756000	4.757713000	0.000551000
H	1.247051000	5.206936000	0.882982000
H	1.255520000	5.208428000	-0.876556000
H	-0.276912000	5.007595000	-0.004146000
Br	2.914024000	-1.891233000	-0.000319000
Br	-2.756511000	-2.053520000	0.000173000

O	-2.445530000	1.008087000	0.000436000
H	-2.799428000	2.388782000	-0.000843000
F	-3.263599000	3.284200000	-0.001778000

Cartesian coordinates of the optimized geometries for the ground state S_1 of DBM at B3LYP/TZVP level

C	1.732044000	3.527326000	-0.371306000
C	2.570508000	2.423031000	-0.099109000
C	1.998193000	1.131399000	-0.119847000
C	0.599893000	1.033130000	-0.394741000
C	0.395350000	3.340870000	-0.643816000
H	2.145365000	4.528317000	-0.366743000
H	3.616307000	2.560752000	0.125285000
C	2.708634000	-0.080557000	0.095266000
C	-0.035080000	-0.266618000	-0.328217000
C	0.773778000	-1.448621000	-0.169881000
C	2.120698000	-1.360541000	0.060039000
H	2.730296000	-2.244647000	0.163804000
N	-0.186966000	2.095631000	-0.651630000
C	-0.524885000	4.483531000	-0.951186000
H	-1.349523000	4.521521000	-0.232913000
H	0.000308000	5.438677000	-0.928185000
H	-0.976881000	4.358100000	-1.940177000

O	-1.327804000	-0.355856000	-0.485189000
Si	-2.840738000	-0.658744000	0.327787000
C	-3.803981000	0.992214000	0.430192000
C	-3.708610000	-1.904403000	-0.780819000
H	-3.117935000	-2.815835000	-0.876196000
H	-4.681242000	-2.171325000	-0.361765000
H	-3.871346000	-1.496477000	-1.780030000
Br	4.572135000	-0.038656000	0.435340000
Br	-0.017384000	-3.166747000	-0.351912000
C	-2.416859000	-1.352796000	2.025937000
H	-1.739299000	-0.690779000	2.568597000
H	-3.329049000	-1.456917000	2.618173000
H	-1.951905000	-2.335739000	1.947585000
C	-3.121982000	1.958437000	1.416666000
H	-2.109309000	2.202670000	1.092128000
H	-3.691649000	2.893265000	1.469961000
H	-3.077211000	1.548720000	2.428909000
C	-5.232440000	0.684780000	0.927606000
H	-5.795895000	1.619475000	1.021368000
H	-5.782561000	0.042403000	0.236213000
H	-5.237519000	0.206148000	1.910779000
C	-3.875251000	1.649750000	-0.960023000

H	-4.443113000	2.585169000	-0.897666000
H	-2.877581000	1.883852000	-1.333133000
H	-4.380822000	1.012708000	-1.690407000

Cartesian coordinates of the optimized geometries for the ground state S_1 of DBMO at B3LYP/TZVP level

C	-3.467979000	-0.850334000	-0.083181000
C	-2.648638000	0.307890000	-0.101458000
C	-1.242824000	0.109062000	-0.038185000
C	-0.746890000	-1.206986000	0.037809000
C	-2.902104000	-2.104289000	-0.007135000
H	-4.546511000	-0.751222000	-0.129203000
H	-3.071364000	1.297711000	-0.160288000
C	-0.283980000	1.182817000	-0.047075000
C	0.704485000	-1.470615000	0.105578000
C	1.567977000	-0.294671000	0.088596000
C	1.090082000	0.999195000	0.014234000
H	1.761626000	1.844290000	0.003985000
N	-1.551523000	-2.317376000	0.054351000
C	-3.742863000	-3.350427000	0.014045000
H	-3.553487000	-3.928181000	0.925058000
H	-4.808710000	-3.121933000	-0.037078000
H	-3.485643000	-4.003643000	-0.826649000

Br	-0.886011000	2.997976000	-0.148613000
Br	3.452152000	-0.570567000	0.173812000
O	1.174499000	-2.622277000	0.173378000

Reference:

1 Y. Y. Bao, B. Liu, H. Wang, J. Tian, R. K. Bai, *Chem. Commun.*, **2011**, *47*, 3957-3959.

2 P. Ros, G. C. A. Schuit, *Theor. Chim. Acta* **1966**, *4*, 1-12.