Beryllium-based fluorenes as efficient anion sponges

M. Merced Montero-Campillo,^[a] Inés Corral, ^[b] Otilia Mó, ^[b] Manuel Yáñez^[b], Ibon Alkorta, ^[b] and José Elguero^[b]

^[a] Instituto de Química Médica, CSIC, C/ Juan de la Cierva, 3, 28006 Madrid. Spain

^[b] Departamento de Química, Facultad de Ciencias, Módulo 13, and Institute of Advanced Chemical Sciences (IadChem) Universidad Autónoma de Madrid. Campus de Excelencia UAM-CSIC, Cantoblanco, 28049 Madrid. Spain

*email: <u>manuel.yanez@uam.es</u>

Supporting Information (A total of 7 pages)



Figure S1. Correlation between the Anion Affinities of 4,5-bis(BeX)-fluorene derivatives calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level of theory (AA(DFT)) and those calculated using the G4MP2 ab initio approach (AA(G4MP2)). This linear correlation fulfills the equation AA(DFT) = 1.056 AA(G4MP2) + 31.02 (r² = 0.996).

Additional anionic complexes for polyatomic anions

For the -polyatomic anions NO_2^- , NO_3^- and SO_4^- , besides the complexes A1- A2- and A3-type already mentioned in the manuscript, other stationary points, namely A4- and A5-type complexes have been found. In these complexes, each beryllium atom interacts with a different oxygen atom of the anion. The only difference is that in A4-type anions the two Be-substituents are on the same side with respect to the fluorene plane, whereas in A5-type complexes the substituents lie one below and the other above the fluorene plane. All these stationary points have been found to be local minima of the PES with the only exception of $A5(Cl,SO_4)$ and $A5(F,SO_4)$ complexes, which present one imaginary frequency. All of them lie higher in energy than the A1-, A2-local minima.



Figure S2. Additional stationary points for the anionic complexes involving polyatomic NO_2^- , NO_3^- and SO_4^- anions. The structures $A5(Cl,SO_4^-)$ and $A5(F,SO_4^-)$ are transition states.



Figure S3. ELF for the 4,5-bis(BeCl)-fluorene complexes with F^- and the 4,5-bis(BeF)-fluorene complexes with Cl⁻. Disynaptic basins involving heavy atoms are shown as green lobes and those corresponding to C-H bonds by yellow ones. Red lobes correspond to monosynaptic basins associated with lone-pairs. The populations of the most significant basins are shown.

Figure S3 shows that the population of the monosynaptic basin of the atom which is chelated between the two Be atoms, does not change significantly when this atom is F or Cl, but what changes dramatically is the volume of the basin, which decreases dramatically on going from Cl to F, favoring the stability of the A2 complex in the case of the 4,5-bis(BeCl)-fluorene interacting with F⁻, and of the A1 complex in the case of the 4,5-bis(BeF)-fluorene interacting with Cl⁻. In summary, in the first case the chelation of the anion is the favored structure whereas in the second it is the chelation of the substituent that leads to the most stable arrangement.



Figure S4. Optimized geometries of the different complexes with the CN^- anion. In all cases the A1-type isomers are the most stable ones due to the large volume of this anion, that when chelated by the two Be atoms distorts significantly the structure of the fluorene molecule.



Figure S5. Molecular graphs of the complexes of 4,5-bis(BeX)-fluorene (X = H, F, Cl) derivatives with NO_2^- . Yellow and red spheres correspond to BCPs and RCPs, respectively. Electron densities are in atomic units.

An inspection of Figure S5 shows that for 4,5-bis(BeX)-fluorene derivatives in which X = H, F exhibit a totally different behavior with respect to the derivatives in which X = Cl, when interacting with NO₂⁻ anions. In the first two cases, the electron density redistribution is not dramatically large. Although the bonds between the O and the Be are weaker in the A1 form because two oxygens interact with the same Be atom, this is counterbalanced by the fact that the ligand (H or F) in the A2 form interacts with both Be atoms. As a result, the A2 form becomes slightly more stable than the A1 structure. The situation is totally different when X = Cl, because this second row atom is so large that forming the chelated A1 form leads to a significant distortion of the fluorene moiety. This A1 structure contains rather weak Cl-Be contacts unlike in the A2 form, in which the atom chelated between the two Be atoms is one of the O atoms of the anion.



Figure S6. Correlation between the calculated gas-phase anion affinities (AAs) and aqueous solution anion affinities of 4,5-bis(BeCl)-fluorene for F⁻, NO₂⁻, and SO₄⁼. All values are in kJ mol⁻¹. The points fit reasonably well a linear correlation which fulfills the equation: AA(gas-phase) = 0.996 AA(aqueous solution) – 209.4, $r^2 = 0.884$.

Table S1. Relative enthalpies (in kJ mol⁻¹) of the different neutral conformers of 4,5bis(BeX)-fluorene (X = H, F, Cl, CN, NO) derivatives with respect to the asymmetric conformer.

Х	C_2	C_{2v}	Asymmetric
Н	37.0 [52.1](TS)	50.3 [41.6]	0.0
F	30.9 (TS)	67.9 [66.2]	0.0
Cl	-2.2 [11.7]	18.2 [4.7]	0.0
CN	1.4	-18.4	0.0
NC	0.9	0.0	_a

^a For the NC substituent the C_1 asymmetric structure does not exist as it collapses to the C_2 local minimum, which are almost degenerate for the CN substituent.