

Supporting Information

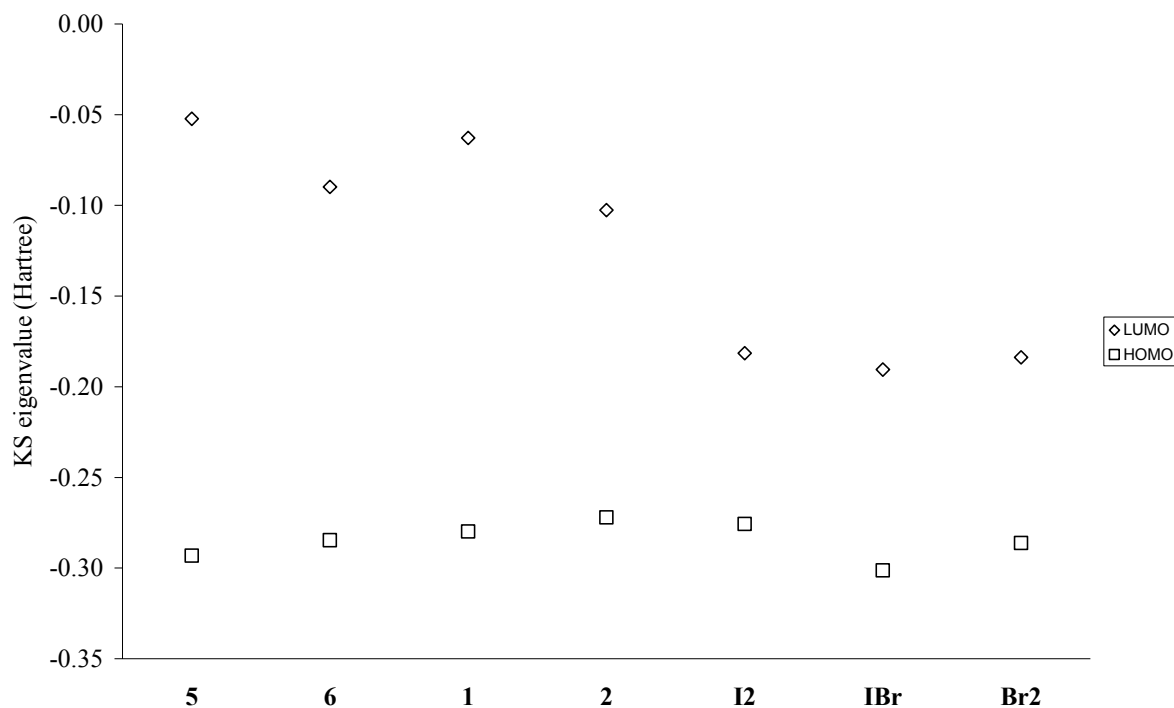


Figure S1. Kohn-Sham HOMO and LUMO eigenvalues calculated for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se (**1**), (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**2**), (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S (**5**), and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**6**), I₂, IBr and Br₂ (Functional B3LYP; Ahlrichs, Horn and Schafer pVDZ basis sets for H, B, C, S and Se; LanL2DZ with relativistic effective core potentials for I and Br).

Table S1. Selected optimized^a and average experimental^{b,c} bond lengths (Å), angles (deg), and dihedrals (°) for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se (**1**), (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**2**), (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S (**5**), and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**6**).

	Optimized				Experimental			
	1	2	5	6	1 ^a	2 ^a	5 ^b	6 ^b
C-E	1.963	1.971	1.814	1.819	1.935	1.952	1.788	1.788
C-C	1.715	1.716	1.723	1.728	1.706	1.702	1.711	1.711
E-E	-	2.344	-	2.087	-	2.301	-	2.030
C-CH₃	1.517	1.518	1.516	1.517	1.513	1.517	1.519	1.526
C-E-C	110.99	-	113.61	-	110.11	-	113.12	-
E-C-C	118.96	117.50	118.39	116.76	117.59	116.75	117.29	116.06
C-E-E	-	104.08	-	105.88	-	102.70	-	105.70
C-C-CH₃	119.51	120.00	119.00	119.50	118.9	119.10	118.33	118.42
C-C-E-C	96.06	-	96.79	-	96.39	-	97.56	-
C-E-E-C	-	103.32	-	105.86	-	99.1	-	105.10
E-C-C-CH₃	11.62	5.89	12.19	6.09	11.6	5.1	12.29	4.09
C-C-E-E	-	107.94	-	107.00	-	109.8	-	107.29

^a Calculated at DFT level (B3LYP functional; Ahlrichs pVDZ basis set); ^b this work; ^c See ref. 37.

Table S2. Selected NBO charges (e) and Wiberg bond indexes for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se (**1**), (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**2**), (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S (**5**), and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**6**).^a

	Q_E^b	Q_{C(E)}^b	Q_{C(Me)}	WBI_{C-C}	WBI_{E-E}^b	WBI_{C-C(Me)}
1	0.604	-0.675	-0.454	0.643	-	0.990
2	0.311	-0.674	-0.458	0.644	1.08	0.990
5	0.423	-0.603	-0.452	0.634	-	0.991
6	0.224	-0.608	-0.455	0.630	1.06	0.991

^a Calculated at DFT level (B3LYP functional; Ahlrichs pVDZ basis set); ^b E = Se (**1**, **2**), S (**5**, **6**).