Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Cooperativity in Berilium Bonds

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Table S1. Calculated interatomic distances (Å) with respect to its position along the cluster chain.

C-Be	1H	$(1H)_2$	$(1H)_3$	$(1H)_4$	$(1H)_5$	$(1H)_6$	$(1H)_7$	$(1H)_8$	$(1H)_9$	$(1H)_{10}$
1	1.701	1.738	1.745	1.748	1.750	1.750	1.751	1.751	1.751	1.751
2		1.719	1.755	1.762	1.765	1.767	1.767	1.768	1.768	1.768
3			1.725	1.760	1.767	1.770	1.771	1.772	1.772	1.773
4				1.727	1.762	1.769	1.772	1.773	1.774	1.774
5					1.728	1.763	1.770	1.773	1.774	1.775
6						1.729	1.763	1.770	1.773	1.775
7							1.729	1.764	1.771	1.774
8								1.729	1.764	1.771
9									1.729	1.764
10										1.729

C-Be	1F	$(1F)_2$	$(1F)_3$	$(1F)_4$	$(1F)_5$	$(1F)_6$	$(1F)_7$	$(1F)_8$	$(1F)_9$	$(1F)_{10}$
1	1.706	1.737	1.744	1.748	1.750	1.750	1.751	1.751	1.751	1.751
2		1.716	1.752	1.759	1.762	1.764	1.765	1.766	1.765	1.766
3			1.720	1.757	1.764	1.767	1.769	1.770	1.770	1.770
4				1.722	1.759	1.766	1.769	1.771	1.771	1.772
5					1.723	1.759	1.767	1.770	1.771	1.772
6						1.724	1.760	1.767	1.770	1.772
7							1.724	1.761	1.768	1.771
8								1.724	1.760	1.768
9									1.724	1.760
10										1.724

Cyclic complexes, C-Be distance

$(1H)_4$	1.784	$(1F)_4$	1.797
$(1H)_5$	1.780	$(1F)_5$	1.788
$(1H)_6$	1.783	$(1F)_6$	1.784
$(1H)_7$	1.781	$(1F)_7$	1.781
$(1H)_8$	1.781	$(1F)_8$	1.780
$(1H)_9$	1.781	$(1F)_9$	1.780
$(1H)_{10}$	1.778	$(1F)_{10}$	1.780

Be-N	$(1H)_2$	$(1H)_3$	$(1H)_4$	$(1H)_5$	$(1H)_6$	$(1H)_7$	$(1H)_8$	$(1H)_9$	$(1H)_{10}$
1	1.738	1.713	1.706	1.703	1.702	1.701	1.701	1.701	1.701
2		1.717	1.692	1.685	1.682	1.681	1.680	1.679	1.679
3			1.711	1.685	1.678	1.675	1.674	1.673	1.673
4				1.708	1.683	1.676	1.672	1.671	1.670
5					1.707	1.681	1.674	1.671	1.670
6						1.706	1.681	1.673	1.670
7							1.706	1.680	1.673

8							1.706	1.680
9								1.706

Be-N	$(1F)_2$	$(1F)_3$	$(1F)_4$	$(1F)_5$	$(1F)_6$	$(1F)_7$	$(1F)_8$	$(1F)_9$	$(1F)_{10}$
1	1.750	1.722	1.714	1.710	1.709	1.708	1.708	1.707	1.707
2		1.726	1.697	1.689	1.685	1.684	1.683	1.683	1.682
3			1.718	1.689	1.681	1.678	1.676	1.676	1.675
4				1.714	1.686	1.678	1.674	1.673	1.672
5					1.713	1.684	1.676	1.673	1.672
6						1.713	1.683	1.676	1.672
7							1.712	1.683	1.675
8								1.711	1.683
9									1.711

Cyclic complexes, Be-N distance

$(1H)_4$	1.700	$(1F)_4$	1.706
$(1H)_5$	1.684	$(1F)_5$	1.689
$(1H)_6$	1.679	$(1F)_6$	1.681
$(1H)_7$	1.672	$(1F)_7$	1.673
$(1H)_8$	1.668	$(1F)_8$	1.668
$(1H)_9$	1.666	$(1F)_9$	1.666
$(1H)_{10}$	1.670	$(1F)_{10}$	1.665

Table S2. E_i Interaction energy (kJ mol^{-1}) of the linear and cyclic structures calculated at the B3LYP/6-31+G(d,p) and B3LYP/6-311++G(3df,2p) computational levels.

	X = H				X=F			
	Linear		Cyclic		Linear		Cyclic	
System	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(3df,2p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(3df,2p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(3df,2p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(3df,2p)
$(\mathbf{1X})_2$	-122.6	–119.0			-121.2	–115.3		
$(\mathbf{1X})_3$	-280.4	–274.0			-280.3	–268.4		
$(\mathbf{1X})_4$	-450.5	–441.3	-639.1	–631.6	-451.8	–434.0	-624.8	–607.7
$(\mathbf{1X})_5$	-626.2	–614.4	-860.7	–850.0	-629.4	–605.6	-852.6	–828.1
$(\mathbf{1X})_6$	-804.5	–790.1	-1064.4	–1047.9	-809.9	–780.2	-1066.4	–1034.6
$(\mathbf{1X})_7$	-984.5	–967.5	-1253.6	–1234.6	-991.9	–956.2	-1263.1	–1225.5
$(\mathbf{1X})_8$	-1165.2	–1145.6	-1430.4	–1408.8	-1174.7	–1133.0	-1448.5	–1404.7
$(\mathbf{1X})_9$	-1346.8	–1324.5	-1601.1	–1576.6	-1358.9	–1311.2	-1628.7	–1577.7
$(\mathbf{1X})_{10}$	-1528.3	–1503.5	-1778.6	–1739.0	-1542.9	–1489.2	-1803.3	–1746.1

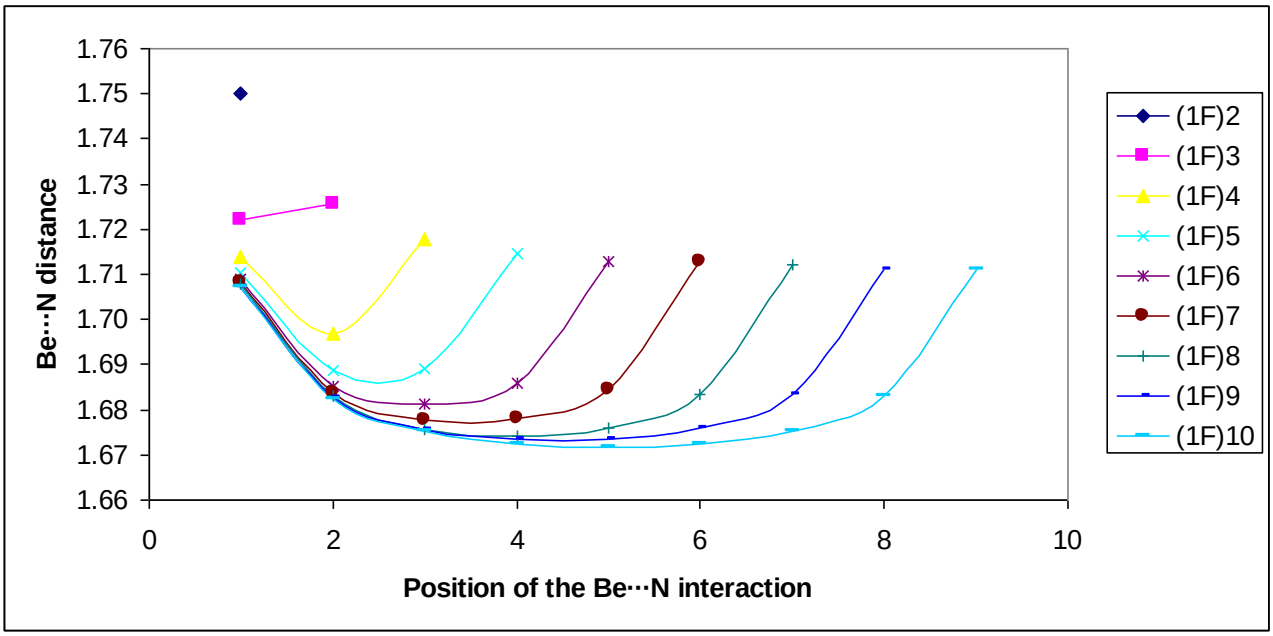

Figure S1. Evolution of the Be···N distance (Å) in the linear chain of the **1**F clusters.

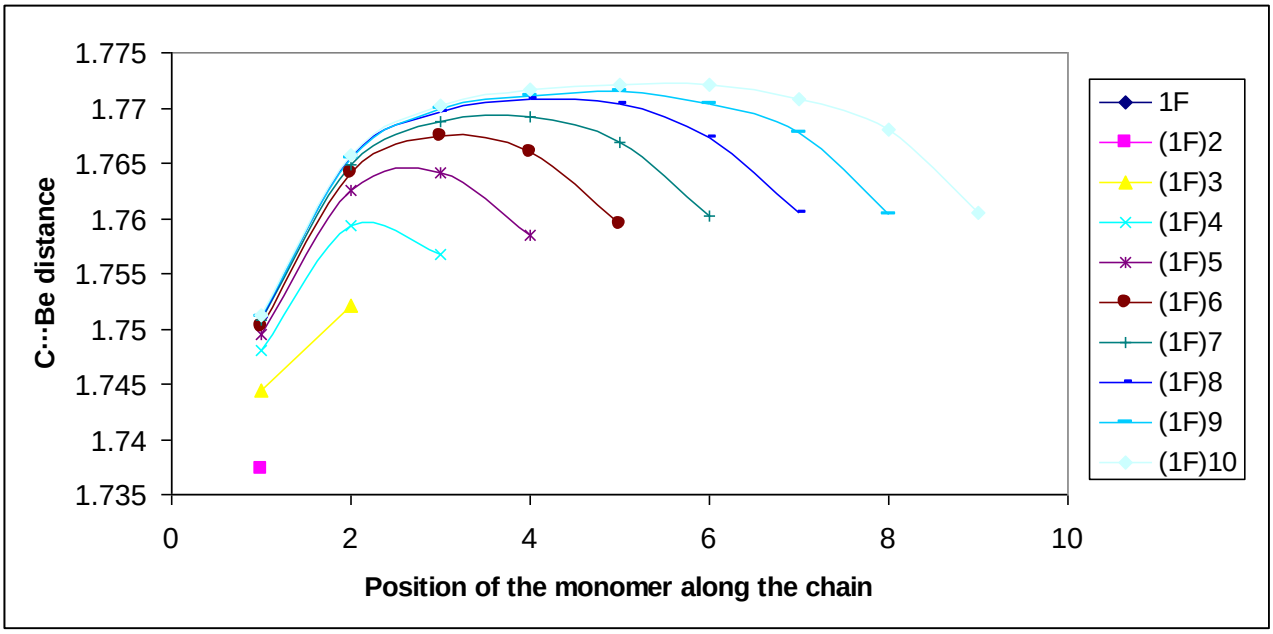

Fig. S2. Evolution of the C-Be distance (Å) in the linear chain of the **1**F clusters

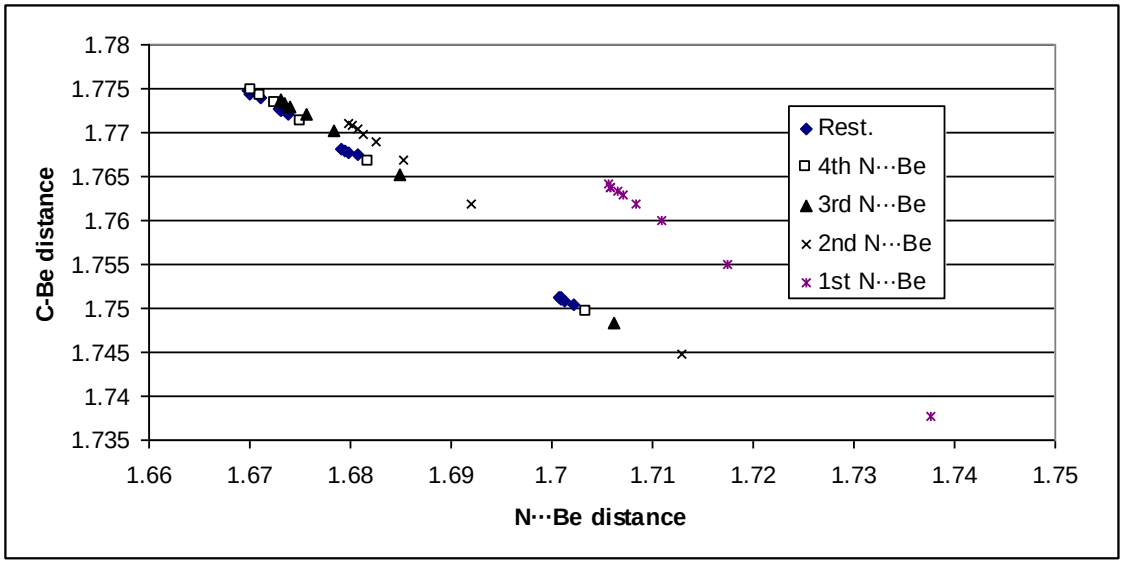

Figure S3. Relationship between the N···Be distance and C-Be distance (Å) based on the interaction position in the chain.

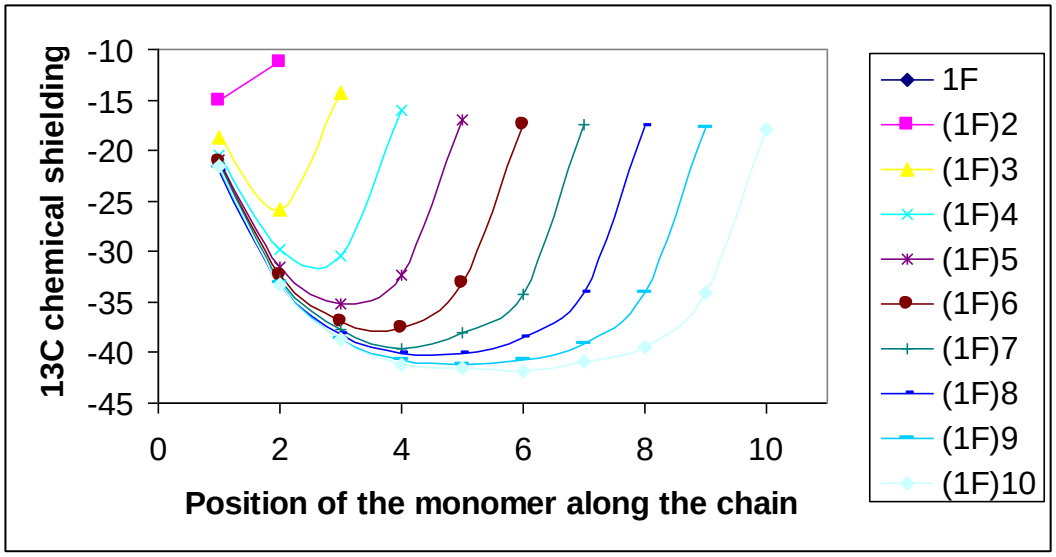

Fig. S4 Absolute chemical shift of the C atoms vs. the position of the monomers in the chain for the **1**F series