Electronic Supplementary Information (ESI†)

for

Unraveling the Stability of Cyclobutadiene Complexes using Aromaticity Markers

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Optimized geometry coordinates

Cartesian coordinates for the optimized structures for equilibrium geometry of Cyclobutadiene-$Fe(CO)_3$ at the B3LYP/cc-pVTZ/LANL2DZ(Fe) level of theory.

Table S1: $CBD-Fe(CO)_3$ equilibrium geometry

	x	y	z
C	-0.68449900	-1.75302900	0.73004100
C	0.76222300	-1.76969100	0.71769000
C	0.76222300	-1.76969100	-0.71769000
C	-0.68449900	-1.75302900	-0.73004100
H	-1.43344700	-1.89352700	1.48788200
H	1.52606300	-1.84524600	1.47126800
H	1.52606300	-1.84524600	-1.47126800
H	-1.43344700	-1.89352700	-1.48788200
Fe	0.00960100	0.01001200	0.00000000
C	0.76222300	0.90499500	-1.34213200
C	-1.57459000	0.81315500	0.00000000
C	0.76222300	0.90499500	1.34213200
O	1.23922300	1.46341500	2.21789900
O	-2.61178200	1.29204500	0.00000000

Cartesian coordinates for the optimized structures for equilibrium geometry of Cyclobutadiene-CH^+ and Cyclobutadiene-CO at the CCSD(T)/cc-pVTZ level of theory.

Table S2: $CBD-CH^+$ equilibrium geometry

	x	y	z
C	-0.0000073586	-0.0000026713	0.9012273640
C	-0.7329024065	-0.7303613332	-0.2778210408
C	-0.7303745655	0.7328986239	-0.2778244685
C	0.7328902309	0.7303835137	-0.2777748281
C	0.7303695759	-0.7328941142	-0.2777728289
H	-1.4881725795	-1.4830245770	-0.1336485665
H	-1.4830394594	1.4881651841	-0.1336396519
H	1.4881535281	1.4830489066	-0.1335777535
H	1.4830344484	-1.4881597331	-0.1335876646
H	-0.0001694137	0.0000162005	1.9739034388

Table S3: CBD-CH$^+$ separation geometry

	x	y	z
C	-0.692725554	0.758109925	-0.6163073572
C	0.692725554	0.758109925	-0.6163073572
C	0.692725554	-0.758109925	-0.6163073572
C	-0.692725554	-0.758109925	-0.6163073572
C	0.000000000	0.000000000	1.9427182848
H	-1.465363501	1.532503483	-0.6456952366
H	1.465363501	1.532503483	-0.6456952366
H	1.465363501	-1.532503483	-0.6456952366
H	-1.465363501	-1.532503483	-0.6456952366
H	0.000000000	0.000000000	3.0802176933

Table S4: CBD-CO equilibrium geometry

	x	y	z
C	0.0000000000	0.0000000000	0.5744281371
C	0.0000000000	1.0453716267	-0.6933181057
C	1.0453716267	0.0000000000	-0.6933181057
C	0.0000000000	-1.0453716267	-0.6933181057
C	-1.0453716267	0.0000000000	-0.6933181057
H	0.0000000000	2.1183400143	-0.5085703661
H	2.1183400143	0.0000000000	-0.5085703661
H	0.0000000000	-2.1183400143	-0.5085703661
H	-2.1183400143	0.0000000000	-0.5085703661
O	0.0000000000	0.0000000000	1.8075092225

Table S5: CBD-CO separation geometry

	x	y	z
C	0.0000000000	0.0000000000	2.4728907043
C	-0.6775527873	0.7906618259	-1.5121881459
C	0.6775527873	0.7906618259	-1.5121881459
C	0.6775527873	-0.7906618259	-1.5121881459
C	-0.6775527873	-0.7906618259	-1.5121881459
H	-1.4518170220	1.5626906959	-1.5098243123
H	1.4518170220	1.5626906959	-1.5098243123
H	1.4518170220	-1.5626906959	-1.5098243123
H	-1.4518170220	-1.5626906959	-1.5098243123
O	0.0000000000	0.0000000000	3.6117411227

Table S6: CBD-Be equilibrium geometry

	x	y	z
Be	0.0000000000	0.0000000000	0.7837154229
C	0.0000000000	1.0500495669	-0.6122913591
C	1.0500495669	0.0000000000	-0.6122913591
C	0.0000000000	-1.0500495669	-0.6122913591
C	-1.0500495669	0.0000000000	-0.6122913591
H	0.0000000000	2.1387466354	-0.6725176304
H	2.1387466354	0.0000000000	-0.6725176304
H	0.0000000000	-2.1387466354	-0.6725176304
H	-2.1387466354	0.0000000000	-0.6725176304

Table S7: CBD-Be separation geometry

	x	y	z
Be	0.0000000000	0.0000000000	2.3192345801
C	-0.6778032939	0.7908005051	-1.6247165667
C	0.6778032939	0.7908005051	-1.6247165667
C	0.6778032939	-0.7908005051	-1.6247165667
C	-0.6778032939	-0.7908005051	-1.6247165667
H	-1.4520025606	1.5629345848	-1.6278994548
H	1.4520025606	1.5629345848	-1.6278994548
H	1.4520025606	-1.5629345848	-1.6278994548
H	-1.4520025606	-1.5629345848	-1.6278994548

Comparison of Wiberg Bond Indices (WBI) of CBD-CH$^+$ and CBD-Fe(CO)$_3$

CBD-CH$^+$	WBI
C1 – C2	1.204
C2 – C3	1.204
C3 – C4	1.204
C4 – C1	1.204
C1 – C5	0.745
C2 – C5	0.745
C3 – C5	0.745
C4 – C5	0.745

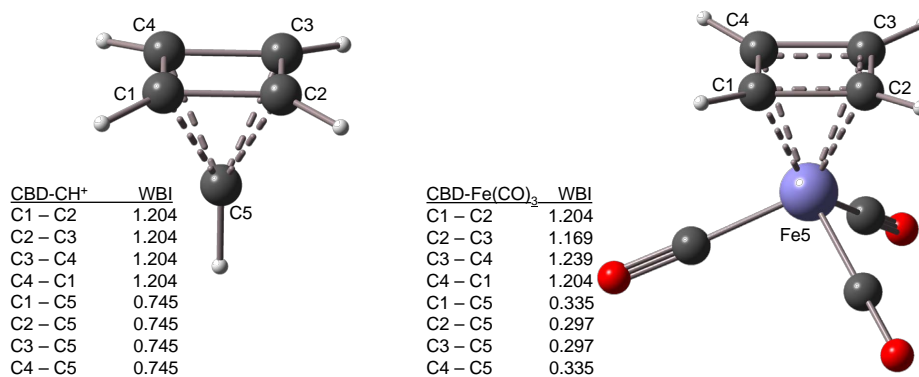| CBD-Fe(CO)$_3$	WBI
C1 – C2	1.204
C2 – C3	1.169
C3 – C4	1.239
C4 – C1	1.204
C1 – C5	0.335
C2 – C5	0.297
C3 – C5	0.297
C4 – C5	0.335

Figure S1: Comparison of Wiberg Bond Indices (WBI) of CBD-CH$^+$ and CBD-Fe(CO)$_3$.

Details of CASSCF-MICD and CASSCF-NICS Computation

The flux of the current density was integrated on a 2D plane perpendicular to the molecular ring plane using a Gauss-Lobatto quadrature grid as described in the paper by Jusélius, Sundholm and Gauss on the GIMIC method. The sign of the integrated ring current susceptibility, referred to as the current strength hereafter, can be used as an indication of aromaticity [1]. A positive value for the integrated MICD denotes aromatic nature, a negative value indicates antiaromaticity. As frames of reference, we note that the current strength for benzene is +13.5 nA/T (CASSCF(6,6)/aug-cc-pVDZ) and for square cyclobutadiene −32.5 nA/T (CASSCF(4,4)/aug-cc-pVDZ).

CASSCF-NICS was computed by the GIAO-MCSCF shielding constant [2] program as implemented in the DALTON program [3] for a dummy atom placed 1 Å above the ring plane opposite to the direction of the approaching CH^+.

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[1] Jusélius, J.; Sundholm, D.; Gauss, J. *J. Chem. Phys.* **2004**, *121*, 3952.

[2] Ruud, K.; Helgaker, T.; Kobayashi, R.; Jørgensen, P.; Bak, K. L.; Jensen, H. J. Aa. *J. Chem. Phys.* **1994**, *100*, 8178.

[3] DALTON, a molecular electronic structure program (see http://www.daltonprogram.org).

Aromaticity along potential energy surface

Table S8: CASSCF(6,7)–MICD values in a.u.[*] with respect to the approach of CH^+ (1.30 - 3.00Å) and the automerization cross-section of cyclobutadiene (1.364 – 1.464 Å for the shorter bond length). Note: Positive values signify aromatic, negative values anti-aromatic.

	1.364	1.384	1.404	1.424	1.444	1.464
1.30	+0.455	+0.470	+0.481	+0.490	+0.496	+0.499
1.50	+0.460	+0.475	+0.487	+0.496	+0.502	+0.505
1.80	+0.442	+0.463	+0.479	+0.491	+0.499	+0.503
2.00	+0.398	+0.434	+0.461	+0.480	+0.491	+0.497
2.10	−0.419	−0.036	+0.237	+0.392	+0.466	+0.490
2.12	−0.933	−0.646	−0.105	+0.262	+0.436	+0.488
2.14	−1.163	−1.215	−0.983	−0.157	+0.344	+0.485
2.16	−1.291	−1.445	−1.589	−1.502	−0.076	+0.480
2.18	−1.388	−1.587	−1.839	−2.147	−2.357	+0.474
2.20	−1.472	−1.699	−2.006	−2.452	−3.155	−4.237
2.25	−1.657	−1.926	−2.311	−2.926	−4.115	−7.511
2.50	−2.607	−2.943	−3.443	−4.322	−6.452	−9.883
2.75	−3.842	−4.163	−4.639	−5.493	−7.794	−8.802
3.00	−5.176	−5.447	−5.846	−6.568	−8.655	−8.627

[*] 1 a.u. current density = 56.358818 nA/T

Table S9: CASSCF(6,7)–NICS(1)$_{zz}$ values taken 1Å opposite to the direction of approach of CH$^+$. Parameters are same as the MICD table. Note: Negative values denote aromatic, positive values anti-aromatic.

	1.364	1.384	1.404	1.424	1.444	1.464
1.30	−11.9	−13.1	−14.0	−14.6	−15.0	−15.1
1.50	−12.5	−13.5	−14.3	−14.8	−15.1	−15.2
1.70	−13.0	−13.9	−14.6	−15.0	−15.3	−15.4
1.90	−13.1	−14.0	−14.7	−15.1	−15.4	−15.5
2.00	−12.1	−13.5	−14.4	−15.1	−15.4	−15.5
2.10	+21.9	+5.3	−6.1	−12.3	−15.1	−15.9
2.12	+43.3	+31.0	+8.0	−7.3	−14.3	−16.2
2.14	+51.8	+54.6	+45.8	+10.54	−10.9	−16.6
2.16	+55.7	+63.0	+71.2	+70.61	+7.7	−17.2
2.18	+58.1	+67.4	+80.4	+98.26	+114.9	−18.1
2.20	+59.8	+70.2	+85.8	+110.09	+150.8	+221.9
2.25	+62.5	+74.6	+93.7	+126.03	+191.0	+383.7
2.50	+65.9	+80.5	+104.9	+151.16	+268.8	–
2.75	+63.4	+77.6	+102.0	+150.69	+291.1	–
3.00	+58.2	+71.1	+93.7	+140.34	+287.2	–

CBD-CO complex

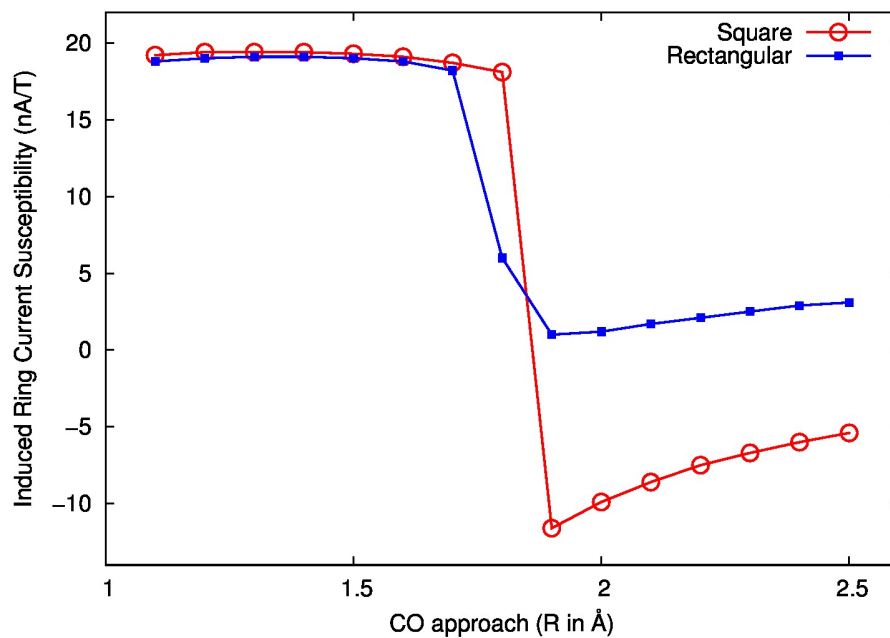CBD-CO system has a similar frontier orbital structure as CBD-CH$^+$

Figure S2: Induced Current strengths of CBD-CO system with respect to the approach of CO separately to Square and Rectangular CBD.
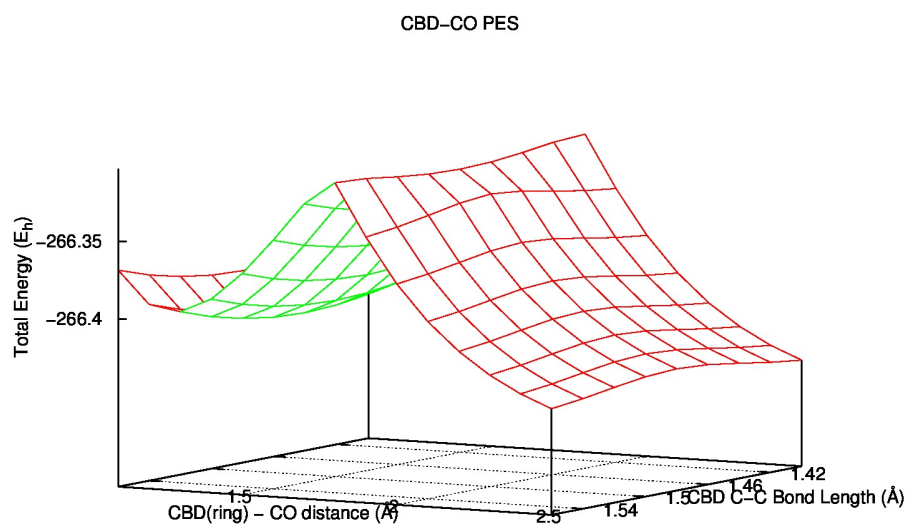
CBD–CO PES

Figure S3: Potential Energy Surface of CBD-CO system with respect to the approach of CO (1.10 - 2.50Å) and the automerization cross-section of cyclobutadiene (1.40 – 1.56 Å for a certain C–C bond length).
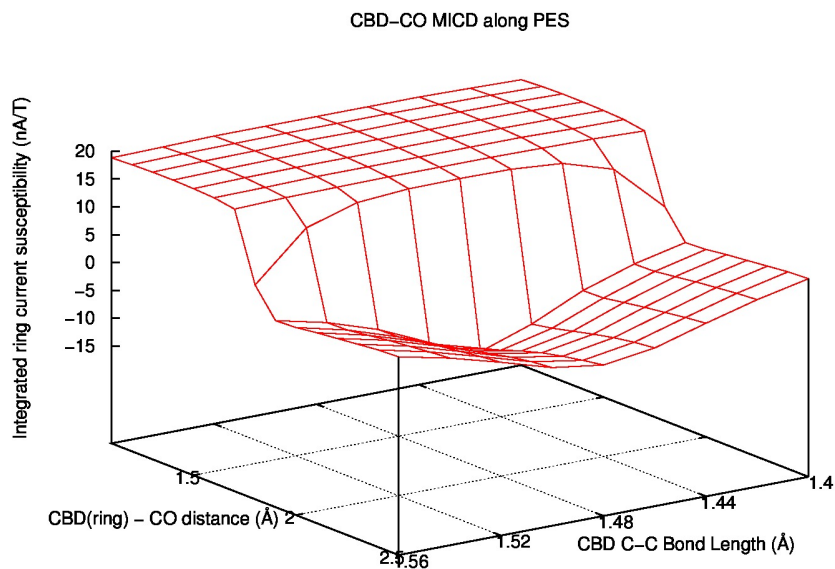
CBD–CO MICD along PES

Figure S4: Induced Current strengths for the CBD-CO system along the PES parameters.
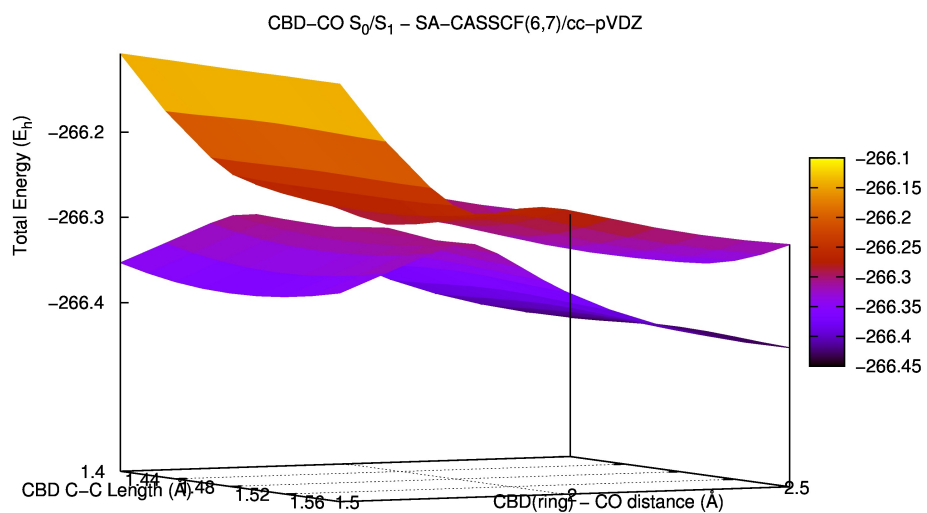
Figure S5: PES for the S_0 and S_1 states of CBD-CO system showing a curve crossing.
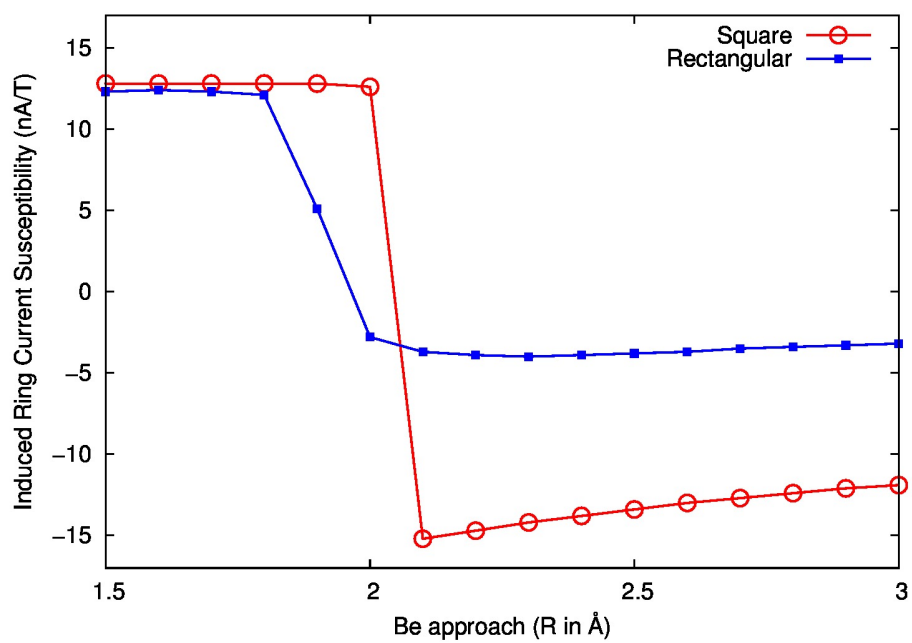
Cyclobutadiene-Be complex

Figure S6: Induced Current strengths of CBD-Be system with respect to the approach of Be atom separately to Square and Rectangular CBD.
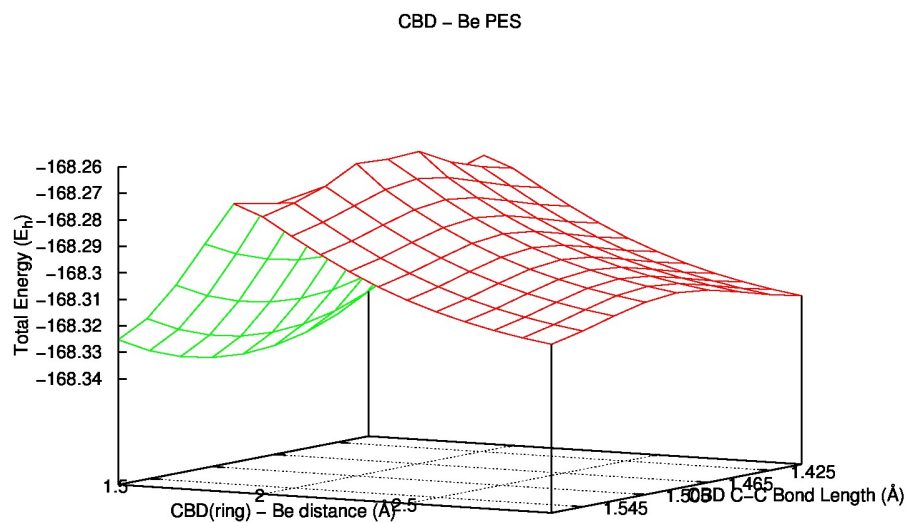
Figure S7: Potential Energy Surface of CBD-Be system with respect to the approach of Be (1.50 - 3.00Å) and the automerization cross-section of cyclobutadiene (1.405 – 1.565 Å for a certain C–C bond length).
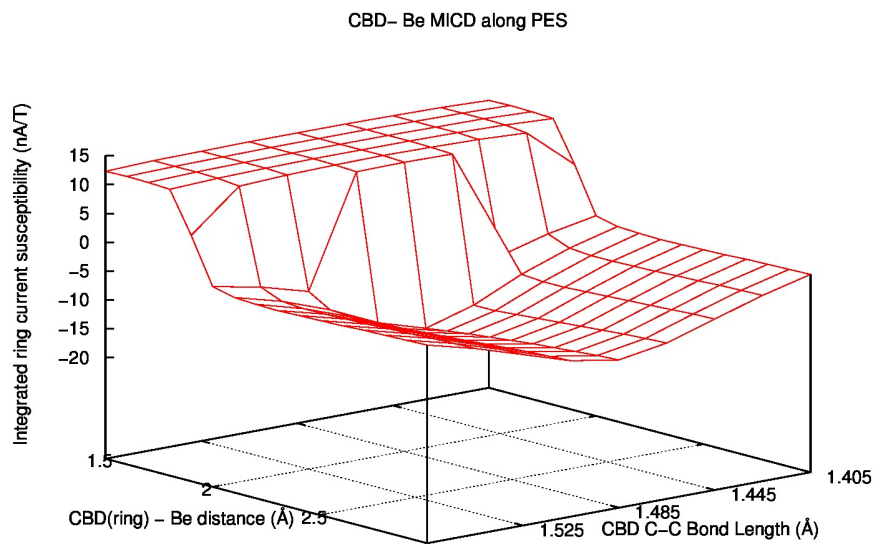

Figure S8: Induced Current strengths for the CBD-Be system along the PES parameters.

Table S10: Wavefunctions of the GS and the first ES of CBD-CH$^+$ at equilibrium, around the CI / avoided crossing and at dissociation (square CBD). Only major configurations are shown in the above wavefunctions and the core electrons are not shown.

CBD-CH$^+$	GS wavefunction	ES wavefunction
Equilibrium	$95\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$	$94\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^1(2b_2)^1\right\rangle - \left|(1a_1)^2(1b_2)^2(1b_1)^1(2b_1)^1\right\rangle\right)$
2.12 Å (before CI)	$55\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-25\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$80\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+8\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
2.22 Å (CI)	$25\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-52\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$80\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+10\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
2.32 Å (after CI)	$75\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+15\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$	$75\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $-15\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
3.00 Å (dissociation)	$50\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+40\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$	$50\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+40\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$

Table S11: Wavefunctions of the GS and the first ES of CBD-Be at equilibrium, around the CI / avoided crossing and at dissociation (square CBD). Only major configurations are shown in the above wavefunctions and the core electrons are not shown.

CBD-Be	GS wavefunction	ES wavefunction
Equilibrium	$95\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$	–
1.92 Å (before CI)	$75\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-10\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$75\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+10\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
2.02 Å (CI)	$74\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+10\%\left(\left|(1a_1)^2(1b_1)^1(2b_1)^1(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^1(2b_2)^1(2a_1)^2\right\rangle\right)$	$72\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-8\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$
2.12 Å (after CI)	$76\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+10\%\left(\left|(1a_1)^2(1b_1)^1(2b_1)^1(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^1(2b_2)^1(2a_1)^2\right\rangle\right)$	$50\%\left(\left|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-25\%\left(\left|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
3.00 Å (dissociation)	$85\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$75\%\left(\left|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$

Table S12: Wavefunctions of the GS and the first ES of CBD-CO at equilibrium, around the CI / avoided crossing and at dissociation (square CBD). Only major configurations are shown in the above wavefunctions and the core electrons are not shown.

CBD-Be	GS wavefunction	ES wavefunction
Equilibrium	$95\%\left(\left\|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$	–
1.77 Å (before CI)	$70\%\left(\left\|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-10\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$82\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+2\%\left(\left\|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle - \left\|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
1.87 Å (CI)	$84\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$ $+2\%\left(\left\|(1a_1)^2(1b_1)^1(2b_1)^1(2a_1)^2\right\rangle - \left\|(1a_1)^2(1b_2)^1(2b_2)^1(2a_1)^2\right\rangle\right)$	$52\%\left(\left\|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-30\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$
1.97 Å (after CI)	$86\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$25\%\left(\left\|(1a_1)^2(1b_1)^2(1b_2)^2\right\rangle\right)$ $-56\%\left(\left\|(1a_1)^2(2b_1)^2(2a_1)^2\right\rangle + \left\|(1a_1)^2(2b_2)^2(2a_1)^2\right\rangle\right)$
3.00 Å (dissociation)	$88\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle - \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$	$82\%\left(\left\|(1a_1)^2(1b_1)^2(2a_1)^2\right\rangle + \left\|(1a_1)^2(1b_2)^2(2a_1)^2\right\rangle\right)$