Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

On the nature of bonding in a new boronyl species $Zn_2(BO)_2$: linear four-center two-electron σ bond

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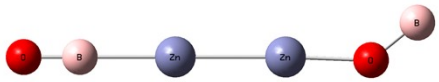
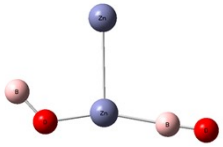
Figure S1. Typical low-lying isomers of $Zn_2(BO)_2$. The values below the structures are relative energies (in eV) in comparison with the linear structure of $Zn_2(BO)_2$, which are calculated by using B3LYP, PBE0, and CCSD(T) methods, respectively.

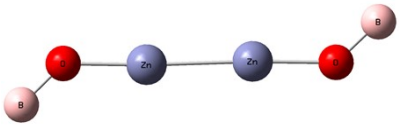
0.00 / 0.00 / 0.00



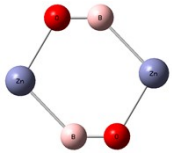
0.96 / 1.00 / 0.85



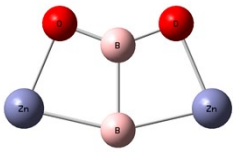
1.11 / 1.24 / 1.05



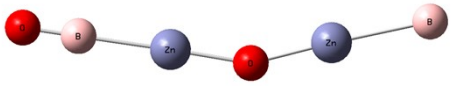
2.04 / 2.09 / 1.79



2.31 / 2.45 / 2.12

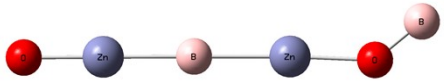


4.21 / 3.93 / 3.98

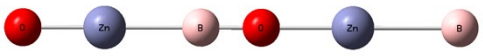


4.63 / 4.69 / 4.25

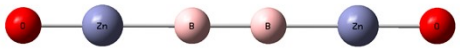
6.25 / 6.39 / 5.67



7.39 / 7.57 / 6.63



7.60 / 7.80 / 7.30



10.71 / 11.11 / 10.10

Figure S2. Representation of the key molecular orbitals (CMOs) of OBZnZnBO ($D_{\infty h}$, $^1\sum_g$), $D_{\infty h}$ HZnZnH, and $D_{\infty h}$ NCZnZnCN from DFT calculations.

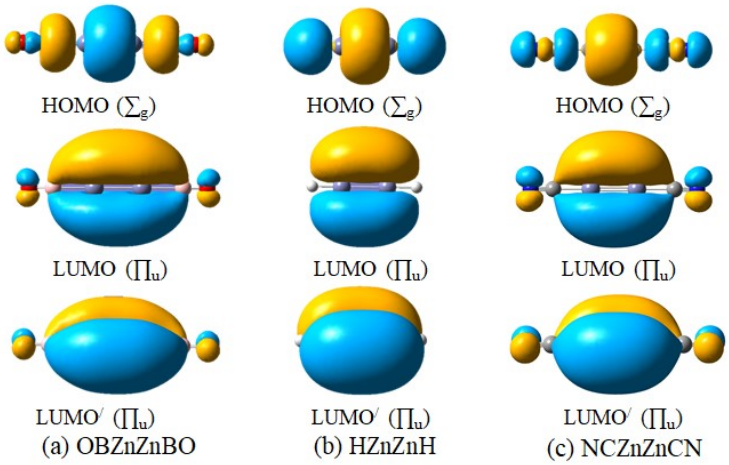


Figure S3. AdNDP bonding pattern for OBZnZnBO ($D_{\infty h}$, $^1\sum_g$) cluster based on 2c-2e Zn-Zn bond.

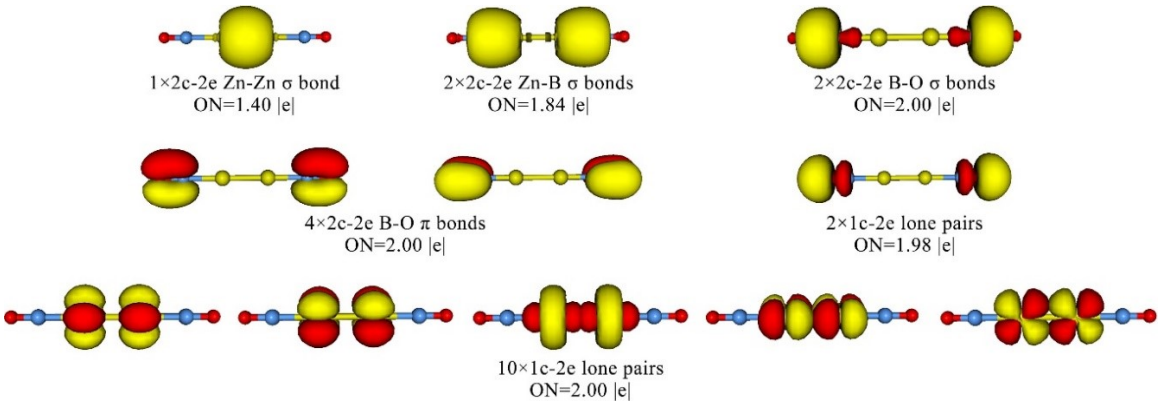


Table S1. The calculated bond length (in Å) of compounds containing Zn-Zn bond using different basis set with B3LYP method.

Basis Set		**$Zn_2(5\text{-}C_5Me_5)_2$**	**HZnZnH**		**NCZnZnCN**		
B,O,H,C,N	**Zn**	**Zn-Zn**	**Zn-Zn**	**Zn-H**	**Zn-Zn**	**Zn-C**	**C-N**
aug-cc-pVTZ	Stuttgart RSC1997 ECP	**2.306**	**2.415**	**1.561**	**2.350**	**1.925**	**1.155**
aug-cc-pVTZ	Lanl2TZ	2.461	2.592	1.635	2.521	2.011	1.156
aug-cc-pVTZ	ECP28MWB	2.401	2.515	1.591	2.440	1.955	1.156
aug-cc-pVDZ	Stuttgart RSC1997 ECP	2.305	2.416	1.563	2.349	1.924	1.166
6-311+G**	Stuttgart RSC1997 ECP	2.306	2.413	1.563	2.350	1.924	1.159

Table S2. Calculated frequencies, intensities and bond lengths for zinc complexes with boronyl as ligands, $D_{\infty h}$ HZnZnH and NCZnZnCN clusters. Bond distances are labeled in Å, frequencies in cm^{-1}.

Species	B3LYP	PBE0
HZnZnH	r_{Zn-H}= 1.561 r_{Zn-Zn}= 2.414 **1844.9** (0), 1816.9 (1029), 436.2 (0), 436.2 (0), 338.2 (94), 338.2 (94), 232.5 (0)	r_{Zn-H}= 1.559 r_{Zn-Zn}= 2.410 1861.1 (0), 1834.2 (951), 437.4 (0), 437.4 (0), 340.5 (100), 340.5 (100), 235.0 (0)
NCZnZnCN	r_{Zn-C}= 1.925 r_{Zn-Zn}= 2.351 r_{C-N}= 1.155 **2275.1** (0), 2274.6 (85), 473.6 (0), 440.2 (157), 255.9 (0), 255.9 (0), 236.0 (0), 236.0 (0), 207.5 (0), 87.1 (0), 87.1 (0), 42.5 (18), 42.5 (18)	r_{Zn-C}= 1.915 r_{Zn-Zn}= 2.349 r_{C-N}= 1.155 2299.7 (0), 2299.3 (77), 480.4 (0), 448.8 (147), 258.9 (0), 258.9 (0), 238.9 (0), 238.9 (0), 209.1 (0), 87.1 (0), 87.1 (0), 43.2 (18), 43.2 (18)
OBZnZnBO	r_{Zn-B}= 2.062 r_{Zn-Zn}= 2.400 r_{B-O}= 1.207 1951.2 (113), 1951.2 (0), 395.0 (0), 362.1 (92), 290.7 (0), 290.7 (0), 269.6 (11), 269.6 (11), 190.2 (0), 87.2 (0), 87.2 (0), 38.9 (14), 38.9 (14)	r_{Zn-B}= 2.056 r_{Zn-Zn}= 2.396 r_{B-O}= 1.206 1969.4 (0), 1969.3 (117), 399.5 (0), 368.3 (84), 292.2 (0), 292.2 (0), 271.4 (10), 271.4 (10), 191.7 (0), 86.9 (0), 86.9 (0), 38.9 (14), 38.9 (14)
OBZnBO	r_{Zn-B}= 2.021 r_{B-O}= 1.205 1970.8 (0), 1970.6 (114), 441.6 (45), 337.0 (5), 337.0 (5), 336.3 (0), 256.8 (0), 256.8 (0), 67.4 (21), 67.4 (21)	r_{Zn-B}= 2.018 r_{B-O}= 1.204 1988.7 (0), 1988.0 (118), 448.0 (43), 341.5 (0), 336.5 (4), 336.5 (4), 257.7 (0), 257.7 (0), 67.2 (21), 67.2 (21)
ZnBO	r_{Zn-B}= 2.118 r_{B-O}= 1.207 1936.9 (67), 315.7 (21), 182.1 (17), 182.1 (17)	r_{Zn-B}= 2.101 r_{B-O}= 1.206 1956.8 (65), 328.5 (23), 191.5 (18), 191.5 (18)