Supporting Information For

$[S©Cd_5S_5]^{2-}$: A Planar Pentacoordinate Sulfur Dianion Stabilized by a Transition-Metal Framework

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Table S1. The planar hyper-coordinate sulfur (phC) isomers of $[X_5Y_6]^{2-}$ (X = Zn, Cd, Hg; Y = O, S, Se), geometric optimization and lowest vibrational frequencies calculated at PBE0-D3/def-TZVPP level. Imaginary frequencies correspond to out-of-plane mode and cavity-distortion mode, indicating that the cavity is too small or too large to fit the chalcogen atoms. Color represents: No color for true minimum, red for out-of-plane mode, and yellow for cavity-distortion mode.

X/Y	O	S	Se	Te
Zn	26*i*	50*i*	41*i*	35*i*
Cd	29*i*	20	20*i*	25*i*
Hg	17	28*i*	29*i*	31*i*

Table S2. The NPA atomic charge of the lowest-energy phAe structures were computed at the PBE0-D3/def2-TZVPP level. The Q values refer to the atomic charge in |e| of S and Cd atoms.

Q	NPA
Q_S^{center}	-1.36
Q_{Cd}	1.31
$Q_S^{termined}$	-1.71

Table S3. The EDA results of the $Cd_5S_6^{2-}$ clusters considering X and X_5Y_5 in different charges and electronic states as interacting fragments at the PBE0-D3/def2-TZVPP level. Energy values are given in kcal/mol. The variation of total interaction energy, electrostatic energy, exchange energy, correlation energy, and dispersion correction in this stage directly defines ΔE_{int}, ΔE_{els}, ΔE_x, ΔE_{DFTc}, and ΔE_{dc} terms of EDA method, respectively.

Energy	S^{2-} (S, $3s^23p^6$) + Cd_5S_5 (S)	S^- (D, $3s^23p^5$) + $Cd_5S_5^-$ (D)	S (S, $3s^23p^6$) + $Cd_5S_5^{2-}$ (S)
ΔE_{int}	-251.3	-104.9	-214.4
ΔE_{Pauli}	359.3	197.2	372.7
ΔE_{disp}[a]	-2.34(0.03%)	-2.34(0.8%)	-2.34(0.4%)
ΔE_{elstat}[a]	-470.2(90.3%)	-156.9(51.9%)	-213.1(36.3%)
ΔE_{orb}[a]	-138.1(9.7%)	-142.9(47.3%)	-371.7(63.3%)

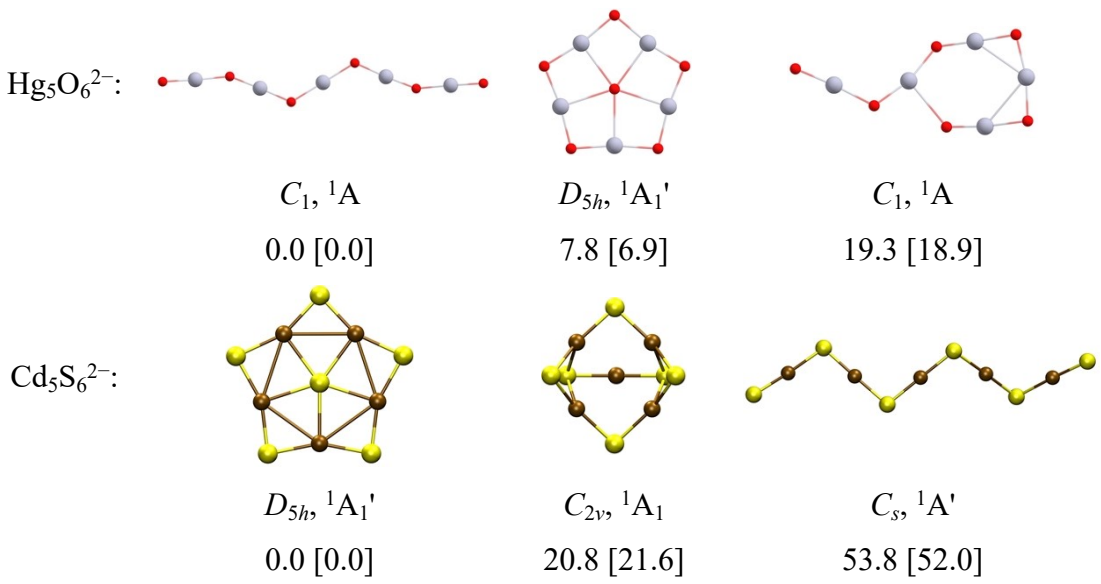

Figure S1. Geometries and relative energies of $Hg_5O_6^{2-}$ and $Cd_5S_6^{2-}$ were calculated at PBE0-D3/def2-TZVPP and PBE-D3/TZ2P-ZORA levels. The latter level includes scalar relativistic effects, whose energies were presented in square bracket.

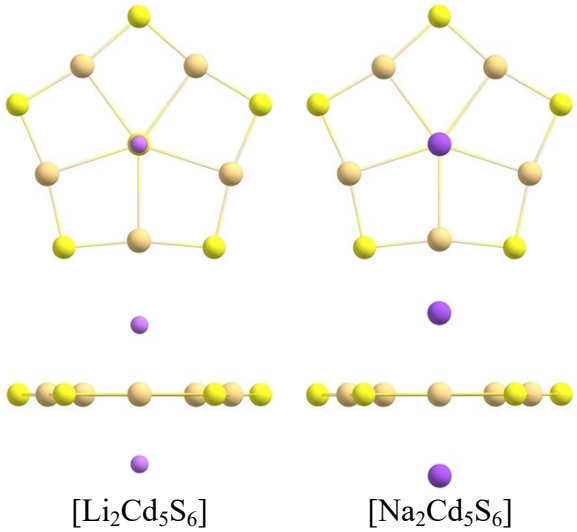

Figure S2. Optimized structures of $[Li^+ \cdot Cd_5S_6^{2-} \cdot Li^+]$ and $[Na^+ \cdot Cd_5S_6^{2-} \cdot Na^+]$ at the PBE0-D3/def2-TZVPP level.

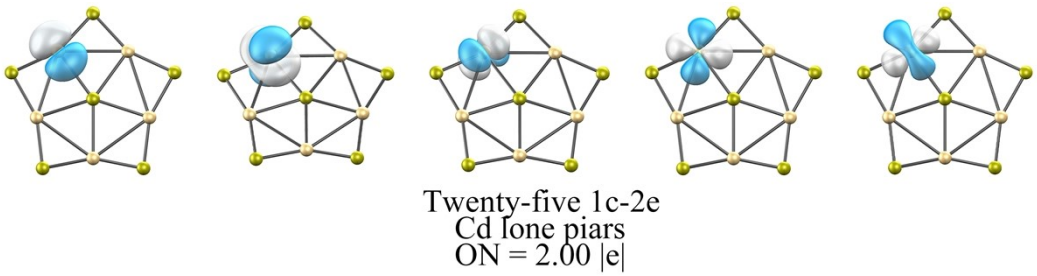

Figure S3. AdNDP view of Cd lone pairs in $Cd_5S_6^{2-}$ calculated at PBE0-D3/def2-TZVPP level. ON denotes the occupation number, which should be close to 2.00 |e| for doubly occupied orbitals.

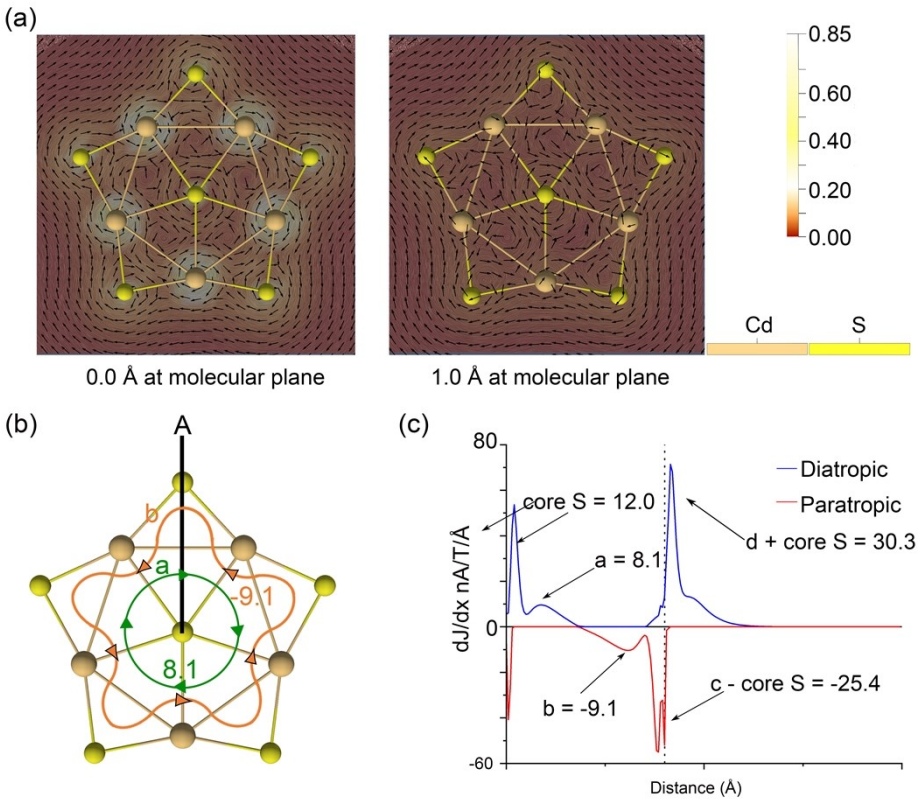

Figure S4. Analysis of magnetically induced current density for $Cd_5S_6^{2-}$. (a) Plot of vectors at 0.0 Å on the molecular plane. (b) Schematic representation of the ring currents and their strength in nA/T, as well as Integration plane used in the analysis and the integration profile resulted from this plane. (c) The numbers in each band (integrated values of the flux in nA/T) identify the different contributions.

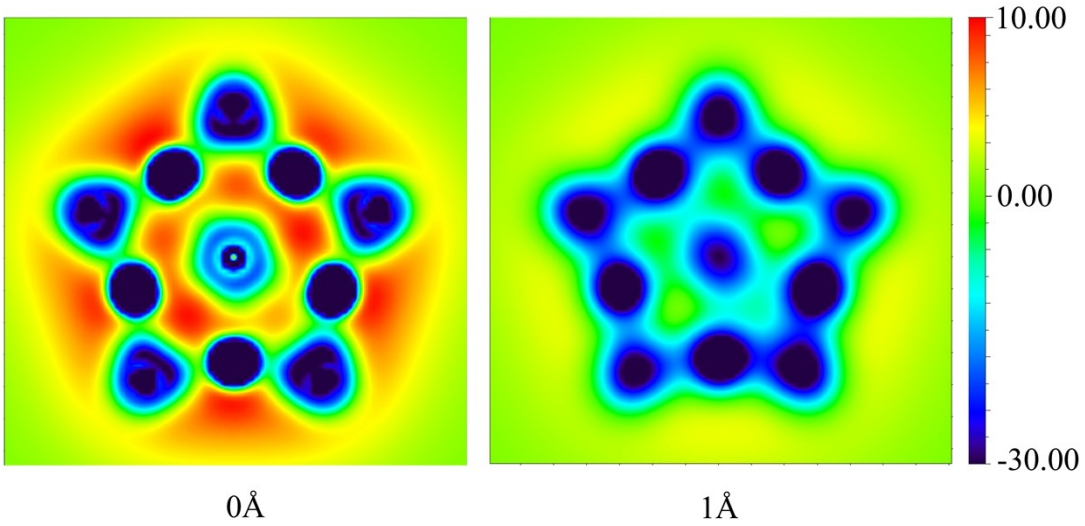

Figure S5. Color-filled map of $NICS_{zz}$ for the D_{5h} geometry of $Cd_5S_6^{2-}$ (Color scale is given in ppm).

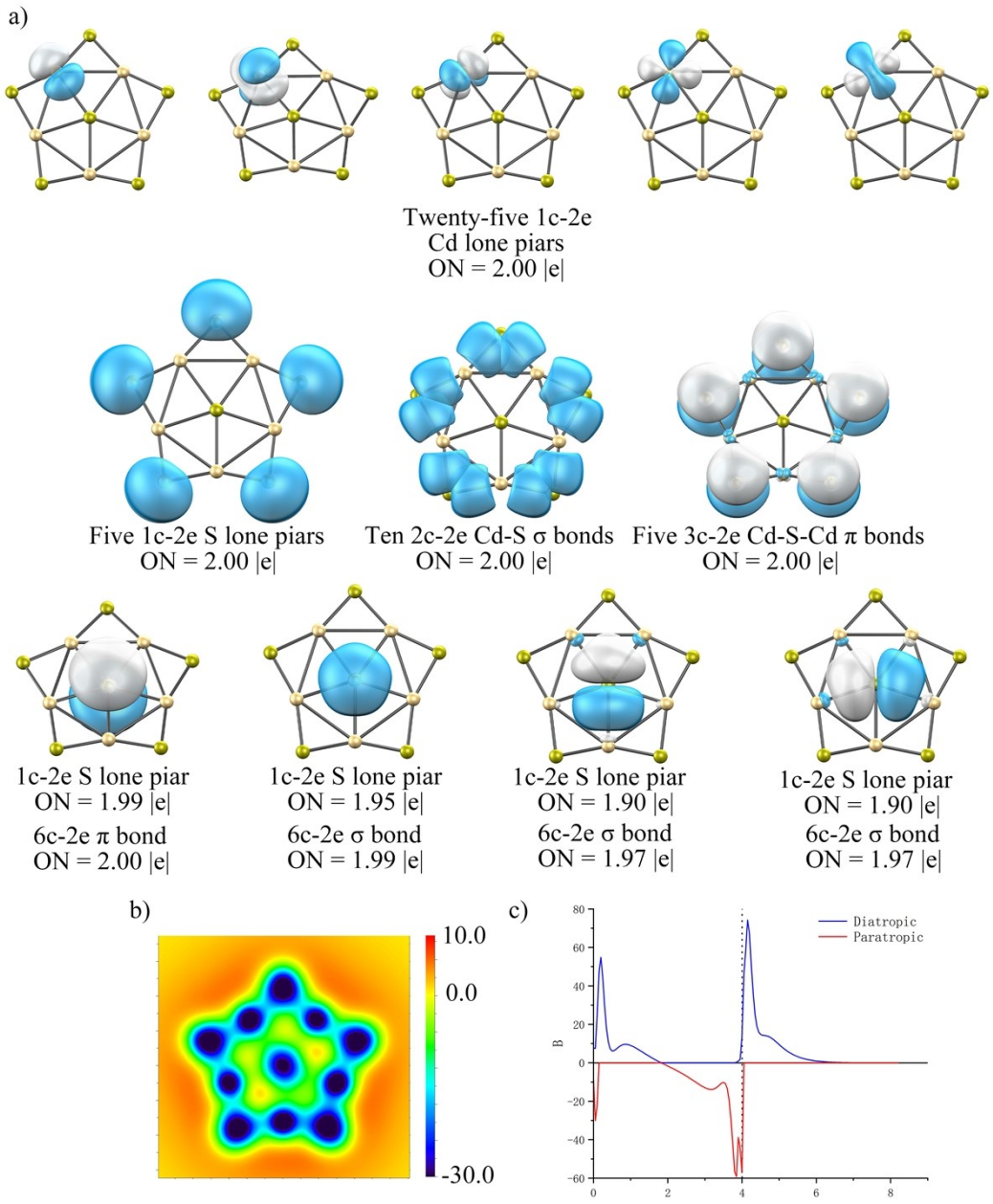

Figure S6. (a) AdNDP view of Cd lone pairs in $Cd_5S_6^{2-}$ cluster. (b) Plot of vectors at 1.0 Å on the molecular plane. (c) Schematic representation of the ring currents and their strength (in nA/T), as well as the integration plane used in the analysis and the resulting integration profile. All calculations were calculated at the PBE0-D3/LanL2TZ(Cd)/def2-TZVPP(S) level.

Cartesian coordinates of low-lying energy isomers of $Cd_5S_6^{2-}$ structures at the PBE0-D3/def2-TZVPP level. Total energy including zero-point corrections and the lowest vibrational frequencies (v_1) are given.

Energy = -3227.7184102 a.u.
Frequencies v_1 = 20.3949 cm^{-1}

S	-0.000000	-4.002910	0.000000
Cd	0.000000	2.774946	-0.000000
S	-2.352851	3.238422	0.000000
S	2.352851	3.238422	0.000000
S	3.806994	-1.236967	0.000000
Cd	1.631072	-2.244978	-0.000000
S	-3.806994	-1.236967	0.000000
Cd	-1.631072	-2.244978	-0.000000
Cd	-2.639130	0.857505	-0.000000
S	0.000000	0.000000	0.000000
Cd	2.639130	0.857505	-0.000000

Energy = -3227.6854674 a.u.
Frequencies v_1 = 26.9259 cm^{-1}

S	-3.165776	0.000000	-0.088660
S	3.165776	-0.000000	-0.088660
S	0.000000	2.889434	-1.972219
S	-0.000000	-2.889434	-1.972219
S	0.000000	-2.296684	1.751029
S	0.000000	2.296684	1.751029
Cd	0.000000	0.000000	2.137016
Cd	-1.541905	-1.749502	-0.482612
Cd	-1.541905	1.749502	-0.482612
Cd	1.541905	1.749502	-0.482612
Cd	1.541905	-1.749502	-0.482612

Energy = -3227.6747944 a.u.
Frequencies v_1 = 18.9170 cm^{-1}

S	-3.920821	-4.699809	-0.000000
S	1.069260	0.752359	3.361625
Cd	0.040904	-0.552822	1.605897
Cd	1.069260	2.389911	1.587487
S	0.183609	-2.487317	-0.000000
S	1.878982	4.006721	0.000000
Cd	-2.006805	-3.518388	-0.000000
S	1.069260	0.752359	-3.361625
S	-0.920858	1.208317	0.000000
Cd	0.040904	-0.552822	-1.605897
Cd	1.069260	2.389911	-1.587487

Energy = -3227.6746939 a.u.
Frequencies ν_1 = 7.2635 cm^{-1}

S	0.000000	0.000000	5.373995
S	-2.365306	2.365306	-1.276237
S	2.365306	2.365306	-1.276237
Cd	0.000000	2.291296	-0.862090
Cd	-0.000000	-2.291296	-0.862090
S	2.365306	-2.365306	-1.276237
S	-2.365306	-2.365306	-1.276237
Cd	0.000000	0.000000	3.119804
Cd	-2.291296	-0.000000	-0.862090
Cd	2.291296	-0.000000	-0.862090
S	0.000000	0.000000	0.716618

Energy = -3227.6733611 a.u.
Frequencies ν_1 = 16.5205 cm^{-1}

S	5.174932	3.178528	-0.000000
S	-1.711252	-3.932715	0.000000
S	-0.336117	-0.855725	3.353968
Cd	-1.345520	-2.157663	1.584779
Cd	-0.336117	0.799164	-1.604815
S	0.567147	2.492888	-0.000000
S	-0.336117	-0.855725	-3.353968
S	-2.191034	-0.023979	0.000000
Cd	2.974088	2.715907	-0.000000
Cd	-0.336117	0.799164	1.604815
Cd	-1.345520	-2.157663	-1.584779

Energy = -3227.6285950 a.u.
Frequencies ν_1 = 10.0709 cm^{-1}

S	1.748214	3.768745	-0.000000
Cd	-2.609679	-2.252631	0.000000
S	-0.794795	-3.160892	1.575416
S	-0.794795	-3.160892	-1.575416
S	1.078966	0.653879	3.489305
S	1.078966	0.653879	-3.489305
Cd	1.078966	2.112835	1.601021
Cd	1.078966	2.112835	-1.601021
Cd	-0.035716	-0.883857	-1.955335
Cd	-0.035716	-0.883857	1.955335
S	-0.747016	0.629308	-0.000000