Supporting Information

Chemical Functionalization of ZnS: A Perspective from the Ligand–ZnS Bond Character

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S1. The relationship between the hydrophobicity and bond ionicity in the context of minerals flotation

It is well known that hydrophobic functionalization of metal sulfides plays a critical role in the realization of efficient mineral separation using the froth flotation technology.[1] The high-performance mineral flotation requires the addition of surfactant molecule (collector), normally composed of a chemically reactive head group and a hydrophobic tail. The collector adsorbs on the mineral surface through the head group, while the tail exposes toward the surrounding aqueous flotation pulp. The induced or enhanced surface hydrophobicity facilitates the attachment of mineral particles to air bubbles and consequently, leads to the separation from hydrophilic minerals.[2–4] As such, various theories have been proposed to consummate the design and screening of more effective collectors for higher flotation performance.

The pioneering Taggart's solubility product theory asserts that the collecting ability of a surfactant is mainly determined by the solubility product of the corresponding metal–ligand compound in solution from the sense of chemical reaction.[5] The basic idea is analogous to the implicit theory of like dissolves like. This theory has been verified to be capable of rationalizing many well-known experimental phenomena in mineral flotation. Despite the widespread acceptance of the solubility product (pK_{sp}) in assessing the collecting capacity, its poor predictive power makes it unsuitable to guide the design of new collectors.

In response, a more advanced model on the basis of the electronegativity theory was advocated by D.Z. Wang et al.[6] They linked the collecting ability of the ligand toward minerals with the relative electronegativity difference [$(\Delta\lambda)^2$] between the ligand head group (e.g., $-OCS_2$, $-NCS_2$ or $-O_2PS_2$) and the active metal atom on mineral surface (e.g., Cu, Pb or Fe). Specifically, a smaller value of $(\Delta\lambda)^2$ indicates a stronger covalent bonding interaction which contributes to a more hydrophobic surface. Conversely, a larger value of $(\Delta\lambda)^2$ represents a weaker covalent bond and a less hydrophobic surface. The relative values of $(\Delta\lambda)^2$ were found to correlate well with the corresponding solubility products. Therefore, the bond ionicity can be taken as a guidance for minerals flotation.

S2. Calculation of the ligand electronegativity

In this study, it was found that the ligand–ZnS(110) bond is highly ionic, and the relative ionicities correlate well with the corresponding experimental solubility product constant of the compounds. This naturally motivates us to use a parameter that can reflect the electronegativity of the ligands to serve as the computational descriptor.

We calculated the electronegativity ($\chi 1$) of the ligands using Gaussian [ub3lyp/6-311++g(3df,3pd)].[7–9] The structures of the ligands optimized in VASP[10–13] were used without further optimizations for the corresponding anion and cation states. The electronegativity was calculated as,[14,15]

$$\chi = \frac{(IE + EA)}{2} \tag{1}$$

$$IE = IE_v = E_{tot}(X^+) - E_{tot}(X) \tag{2}$$

$$EA = EA_v = E_{tot}(X) - E_{tot}(X^-) \tag{3}$$

where χ is the electronegativity, IE is the vertical ionization energy and EA is the vertical electron affinity. For comparison, we also calculated the electronegativity ($\chi 2$) of the ligands which were further optimized in VASP in 30×30×30 cell and with more strict convergence conditions (EDIFF = 1e–6 and EDIFFG = – 0.01). Alternatively, we calculated a parameter in VASP and assumed it as SOMO (i.e., singly occupied molecular orbital). Since for radical with an odd number of electrons, the spin orbitals are separated with different energy levels and each of the occupied ones can only contain one electron. Besides, the orbital energies obtained in VASP cannot be directly used, since the vacuum energy level is not zero due to the periodic boundary conditions. As such, the SOMO defined above was calculated by subtracting the vacuum energy level from the Fermi level of the radical system in a way similar to that of work function. All these results were compared with the electronegativity values calculated by D. Z. Wang et al. using empirical parameters which is denoted as the empirical electronegativity (λ) here, as shown in Figure S1 below.[6]

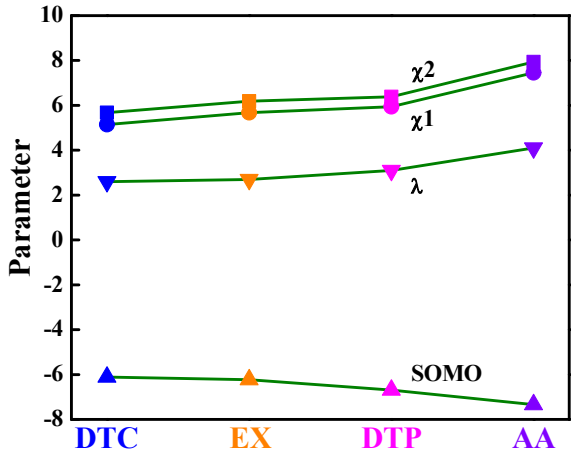

Figure S1. Computational parameters (χ1, χ2 and SOMO) and empirical electronegativity (λ) of the ligands.

Although the different data sources correlate well, we eventually decide to use the electronegativity (χ2) calculated in Gaussian to better reflect the intrinsic attribute of free ligands and to avoid confusions. More suitable parameters may be selected based on specific system and database size.

S3. DFT Calculations for dimethylzinc

Since the Zn–C bond has a significant amount of covalence, we constructed the dimethylzinc model and applied the same analytical techniques to verify our conclusions. DFT calculations were conducted with the dimethylzinc [$Zn(CH3)_2$] in a 30×30×30 cell using the same methods. The results are presented in Figure S2 (a)-(f) below. The line profiles along Zn–C bond for the charge density difference map (CDDM) and the electron localization function (ELF) are compared with those of the DTC–ZnS(110) system in Figure S2(c) and (d), respectively, since DTC forms the strongest covalent bond among the four ligands studied. The color scales for CDDM and ELF are identical as those in the manuscript.

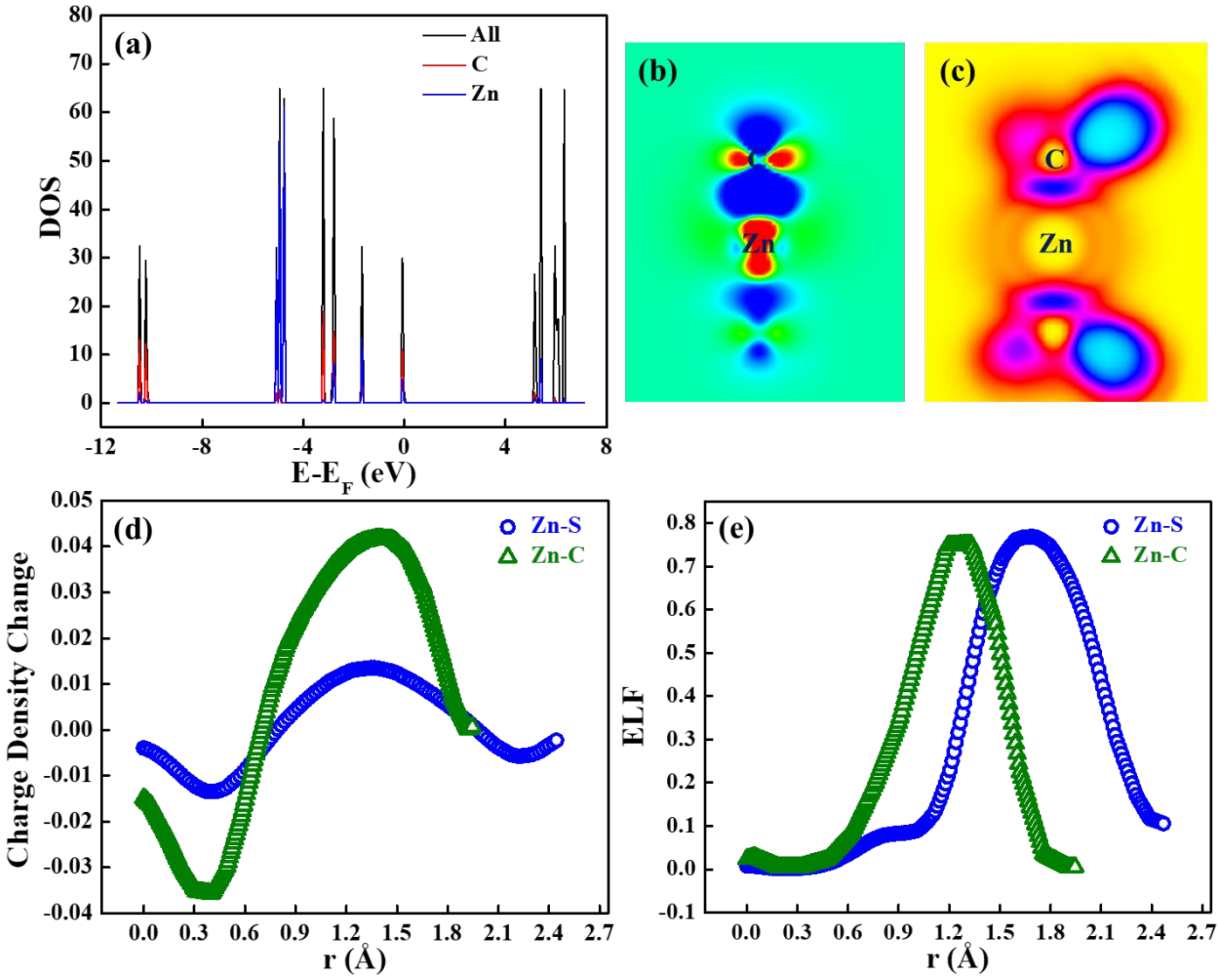

Figure S2. (a) PDOS, (b) charge density difference map (CDDM), (c) electron location function (ELF) of dimethylzinc; (c) the line profiles of CDDM along Zn–C for dimethylzinc (green) and Zn–S for DTC–ZnS(110) (blue), (d) the line profiles of ELF along Zn–C for dimethylzinc (green) and Zn–S for DTC–ZnS(110) (blue).

PDOS in Figure S2(a) shows that the valence electrons of the connected Zn and C are strongly correlated. Moreover, upon binding of the CH_3 radical to CH_3Zn, substantial electron accumulations can be observed in the Zn–C bonding region in Figure S2(b), and the contour indicates slight polarization toward C. In terms of the ELF in Figure S2(c), there is clear localization domain along the Zn–C bond and locates closely to the bond center. Overall, these results suggest that the Zn–C bond in dimethylzinc is strongly covalent with slight polarization.

Apparently, the results for dimethylzinc are very different from the ligand–ZnS(110) systems. By examining Figure S2(d), we can see that the electron accumulation within the bonding area is much

stronger than that of the DTC–ZnS(110). Moreover, for the ELF in Figure S2(e), the localization domain locates more closely to the Zn in dimethylzinc along the bond, while this domain is much more stretched toward S in DTC–ZnS(110). Therefore, the Zn–C bond possess considerably larger fractions of covalency than Zn–S in the ligand–ZnS(110) systems which further verified our analytical techniques and confirmed the applicability of our methodology.

S4. Models

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0.0000000000 0.0000000000 30.0000000000
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0.375000000	0.666670045	0.097319997
0.374641814	0.665469403	0.194447324
0.125503468	0.833141185	0.145731578
0.125000000	0.833329955	0.048659999
0.123351752	0.830349177	0.245711097
0.875000000	0.666670045	0.000000000
0.875000000	0.666670045	0.097319997
0.878073837	0.667625021	0.192763819

0.624072614 0.833887697 0.146010955
0.625000000 0.833329955 0.048659999
0.621371427 0.833742185 0.245293330
0.381449141 0.349454304 0.286303910
0.379080053 0.653524538 0.289043945
0.372074296 0.499996498 0.312356300
0.487898667 0.503427615 0.336973483
0.262378417 0.493572821 0.339405779
0.516234827 0.406697012 0.358855105
0.135468827 0.490631428 0.329058519
0.446583472 0.399239875 0.378720514
0.520914931 0.326222922 0.344194526
0.114009582 0.566054814 0.313320289
0.116416260 0.411171928 0.314847267
0.605892080 0.426177908 0.369863956
0.081471278 0.492744900 0.352316894

aa_ZnS(110)
1.0
10.9123001099 0.0000000000 0.0000000000
0.0000000000 11.5741996765 0.0000000000
0.0000000000 0.0000000000 39.6451988220
Zn S O H C
36 36 2 5 3
Direct
0.250000000 -0.000000000 0.048659999
0.250660549 0.999318333 0.145488800
0.217177665 0.997313625 0.232796374
-0.000000000 0.166669993 0.000000000
0.006576950 0.166567163 0.196854291
-0.000000000 0.166669993 0.097319997
0.750000000 -0.000000000 0.048659999
0.751045500 0.999084327 0.145616028
0.717985495 0.998549161 0.231171035
0.500000000 0.166669993 0.000000000
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0.500000000 0.166669993 0.097319997
0.250000000 0.333329996 0.048659999
0.250377478 0.332021683 0.145760600
0.233188697 0.345252368 0.239976162
-0.000000000 0.500000000 0.000000000
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0.750000000 0.333329996 0.048659999
0.747101564 0.331098162 0.144636860
0.718678358 0.331220747 0.231031177
0.500000000 0.500000000 0.000000000
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0.250000000 0.666670045 0.048659999
0.250427446 0.666644749 0.145787542

0.233179324	0.647205834	0.239735923
0.000000000	0.833329955	0.000000000
0.006646614	0.829977816	0.196961733
0.000000000	0.833329955	0.097319997
0.750000000	0.666670045	0.048659999
0.747300910	0.667344996	0.144690648
0.718508245	0.665646474	0.231044480
0.500000000	0.833329955	0.000000000
0.498880696	0.829576627	0.196777362
0.500000000	0.833329955	0.097319997
0.375000000	0.000000000	0.000000000
0.375000000	-0.000000000	0.097319997
0.376361562	0.998809946	0.194130252
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0.125000000	0.166669993	0.048659999
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0.875000000	0.000000000	0.000000000
0.875000000	-0.000000000	0.097319997
0.879989611	0.998316885	0.193951282
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0.625000000	0.166669993	0.048659999
0.619637914	0.165143463	0.245446826
0.375000000	0.333329996	0.000000000
0.375000000	0.333329996	0.097319997
0.372952698	0.333478578	0.194183126
0.125284600	0.499373127	0.144955592
0.125000000	0.500000000	0.048659999
0.092756992	0.496689759	0.243319021
0.875000000	0.333329996	0.000000000
0.875000000	0.333329996	0.097319997
0.875096221	0.328872795	0.192318485
0.623841762	0.499292049	0.145790886
0.625000000	0.500000000	0.048659999
0.622566327	0.498425566	0.245021265
0.375000000	0.666670045	0.000000000
0.375000000	0.666670045	0.097319997
0.373194475	0.663825633	0.194245056
0.124875518	0.832949118	0.145766434
0.125000000	0.833329955	0.048659999
0.125049859	0.825495854	0.245359746
0.875000000	0.666670045	0.000000000
0.875000000	0.666670045	0.097319997
0.875195327	0.667934173	0.192395161
0.622726783	0.833752073	0.146084432
0.625000000	0.833329955	0.048659999
0.619665662	0.831933828	0.245472854
0.335421114	0.394550069	0.279009403
0.335054909	0.591582589	0.278397005
0.369272606	0.605741780	0.374597063
0.277759423	0.658494534	0.340764827
0.439285774	0.666051041	0.337966940

0.292320821	0.437274707	0.341254953
0.451136329	0.447035652	0.335572578
0.362910728	0.612683897	0.347031022
0.364652674	0.493379930	0.330836248
0.343757101	0.493717880	0.293041082

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