Intercluster Reactivity of Metalloaromatic and Antiaromatic Compounds and Their Applications in Molecular Electronics: A Theoretical Investigation

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Local reactivity descriptors, such as the condensed local softness and Fukui function, have been employed to investigate the intercluster reactivity of the metalloaromatic (Al_4Li^- and Al_4Na^-) and antiaromatic (Al_4Li_4 and Al_4Na_4) compounds. We have used the concept of group softness and group Fukui function to characterize the strength of the nucleophilicity (ability to donate electrons) of the Al_4 unit in these compounds. The aim of this work is to understand the enhanced efficiency of the electron injection of the Al−Li cathode in the organic light emitting diode due to the formation of Al−Li clusters at the interface. Our analysis shows that the Al_4 unit of the Al_4Li^- cluster has the highest nucleophilicity compared to the other clusters. Hence, we believe that the formation of the Al_4Li^- type of metalloaromatic clusters would be responsible for the increase in the efficiency of the electron injection of the Al−Li cathode.

1. Introduction

Recently, all-metal atom clusters were shown to have aromaticity and antiaromaticity.[1−13] This opened a new area of metalloaromatic and antiaromatic compounds. Li et al.,[1] for the first time, synthesized the metalloaromatic compounds, viz., Al_4Li^-, Al_4Na^-, Al_4Li_2, etc. These compounds were shown to have aromaticity, according to the basic criteria defined for the aromatic compounds such as planarity, cyclic conjugation, and Huckel's $(4n + 2)$ π electron rule. Motivated by this work, Shetty et al.[9] predicted the possibility of antiaromaticity in the Al_4Li_4 metal cluster using ab initio calculations. Parallel to this, in an interesting experimental and theoretical work, Kuznetsov et al.[10] confirmed the existence of antiaromaticity in $Al_4Li_3^-$ and Al_4Li_4 clusters. As an extension of this work, more metalloantiaromatic compounds were discussed.[13] Very recently, magnetic properties of the metalloaromatic and antiaromatic compounds were investigated.[14−16] Surprisingly, the magnetic properties in these compounds were shown to have a somewhat different trend than the organic aromatic and antiaromatic compounds.[14−16] The metalloaromatic compounds were shown to have a diamagnetic ring current arising from the σ-electron delocalization rather than the conventional π-electron delocalization.[14] Therefore, these metal clusters were said to have σ-aromaticity rather than π-aromaticity. On the other hand, metalloantiaromatic compounds were shown to have a diamagnetic current in the plane due to the σ electrons and a paramagnetic current out of the plane due to π electrons.[15,16] This shows that, only on the basis of the electron counting rule, it is difficult to characterize the existence of metalloaromatic and antiaromatic compounds and the issue remains unresolved.[16,17]

Investigation of the mixed metal clusters has been important in understanding the electronic, stoichiometric, and surface properties of the metal alloys at a microscopic level. The Al−Li alloy forms a very strong and light material and is used for aerospace engineering.[18] More interestingly, in the past decade, Al−Li alloys have been widely used as electron injecting materials in organic light emitting diodes (OLED).[19−21] It has been shown that the efficiency of the OLEDs depends on the number density of electrons and holes in the organic emission layer. This has been achieved by using high work-function material such as indium tin oxide (ITO) for hole injection and Li as a low work-function material for electron injection.[20] Haskal et al. showed that the Li atoms diffuse into the organic layer causing degradation.[19] To avoid this, Al−Li alloys were used as electron injecting devices for OLED. Furthermore, they showed that there is charge transfer from Li to Al atoms at the interface.[19] This kind of bonding arrangement allows the Li−Al atoms to cluster, resulting into the contraction of the interface.[19,21] More importantly, the reason for the high efficiency for the electron injection of the Al−Li alloy was given on account of enhanced charge transfer from the Li to Al and the clustering of Al−Li atoms at the interface. In the past few years, more research has been focused on the study of the interaction of the organic layer with the metal cathodes and anodes. Tris(8-hydroxyquinolinato)aluminum (Alq_3) has been the prototypical electroluminescent molecule for the organic layer in the applications of OLED.[21] Curioni and Andreoni[21] have studied the interaction of the Alq_3 molecule with the metal cathode surfaces, such as Li, Al, and Ca, using ab initio simulations. Their investigation reveals that the Alq_3 accepts the electron from the metal and thus acts as an electrophile, where the oxygen atoms were shown to be the electrophilic centers.[21] Hence, it is clear that the metal that donates the electron would act as a nucleophile. Tang et al., with the help of photoelectron spectroscopy, showed that the metal electronegativity is linearly dependent on the charge injection barrier.[22]

From the work of Haskal et al.[19] it can be inferred that the crucial part for the high efficiency of the Al−Li cathode is the cluster formation of the Al−Li atoms and the charge transfer from the Li to Al atoms at the Al−Li interface. It is also

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important to note that the Al atoms at the interface should have a low work-function (high nucleophilicity) to allow the easy injection of electrons in the organic layer. Hence, a deeper understanding of the formation of the Al-alkali clusters at the interface and the nucleophilicity of the Al in these clusters at the microscopic level is required. Motivated by this, in the present work, we use the approach of local reactivity descriptors[23] to investigate the intercluster reactivity of some Al-alkali clusters which have been shown to be metalloaromatic and antiaromatic compounds. Furthermore, we study the trend of the nucleophilicity of the Al_4 unit in these compounds to clarify the role of Al in the Al-alkali clusters for the applications of OLED's.

Local reactivity descriptors, such as local softness and Fukui function (FF), based on density functional theory (DFT), have been used to determine the site reactivity in a system.[23] Intramolecular reactivity has been studied extensively with use of these descriptors.[24] These descriptors have been well tested for studying the intramolecular reactivity. However, there is considerable ambiguity in using these descriptors for characterizing the intermolecular reactivity.[24b] De Proft et al.[25] have employed the concept of group hardness, softness, and electronegativity to study a series of organic compounds. Recently, Krishnamurty and Pal[26] have used the concept of group softness for studying the intermolecular reactivity in carbonyl compounds and organic acids. The group softness is defined as the summation of the local softness of a group of atoms around the most reactive site in a molecule.[26] These studies have shown that the molecule with the maximum group softness is the most reactive molecule within a series.[25,26] Hence, the reactivity descriptors can be used for investigating the strength of the electrophilicity (electron acceptance) and nucleophilicity (electron donation) of a single site or a group of sites in a molecular system.

In this work we introduce the concept of group FF for comparing the reactivity of the Al-alkali clusters belonging to the class of metalloaromatic and antiaromatic compounds. The group FF is somewhat similar to the group softness defined earlier. However, we have defined group FF as the group softness divided by the total softness. In this paper we apply the concept of group softness and group FF for investigating the intermolecular reactivity of some Al-alkali metal clusters. Moreover, we use these concepts to understand the increase in the electron injection due to the formation of Al-alkali clusters at the interface of the Al−Li cathodes and their applications in molecular electronics.

The present paper has been organized as follows: in section 2, we discuss the theoretical background to calculate the group softness and group FF. This is followed by the computational details of the present study in section 3. In section 4 we present the results and discussion on the structure and reactivity of the Al based alkali clusters. The conclusions are presented in the section 5 of the paper.

2. Theoretical Background

The ground-state energy of an atom or a molecule, in density functional theory, can be expressed in terms of electron density, $\rho(r)$, as[27]

$$E[\rho] = F_{\mathrm{HK}}[\rho] + \int v(r)\rho(r)\,\mathrm{d}r \tag{1}$$

where $v(r)$ is the external potential and $F_{\mathrm{HK}}[\rho]$, the universal Hohenberg−Kohn functional expressed as

$$F_{\mathrm{HK}}[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] \tag{2}$$

is the sum of electronic kinetic energy ($T[\rho]$) and electron−electron interaction energy ($V_{\mathrm{ee}}[\rho]$).

The first and second partial derivative of $E[\rho]$ with respect to the number of electrons N under constant external potential $v(r)$ are defined as chemical potential,[28] μ, and the hardness,[29] η, for a system.

$$\mu = \left(\frac{\partial E[\rho]}{\partial N}\right)_{v(r)} \tag{3}$$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E[\rho]}{\partial N^2}\right)_{v(r)} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{4}$$

Global softness, S, defined as the inverse of hardness, can be written as

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \tag{5}$$

It has been customary to use the finite difference approximation to compute μ and η as[30]

$$\mu \approx \frac{-I - A}{2} \tag{6}$$

$$\eta \approx \frac{I - A}{2} \tag{7}$$

where I and A are ionization potential and electron affinity of a chemical species, respectively.

The principle of maximum hardness was proposed by Pearson [31] relating the hardness and stability of a system at constant chemical potential and later proved by Parr and Chattaraj.[32] The global hardness reflects the overall stability of a system. However, the site selectivity and reactivity can only be studied by using the local reactivity descriptors, such as local softness[23b] $s(r)$, which is defined as

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}\left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \tag{8}$$

and

$$\int s(r)\,\mathrm{d}r = S \tag{9}$$

where $f(r)$ is the Fukui function,[23a]

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)}\right)_N \tag{10}$$

Thus, the Fukui function can be interpreted either as the change of electron density at each point r when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point r.

The N discontinuity problem of atoms and molecules[33] in eq 10 leads to the introduction[23a] of both right- and left-hand-side derivatives at a given number of electrons, N_0 ($=N$)

$$f^{+}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{+}_{v(r)} \tag{11a}$$

for nucleophilic attack and

$$f^{-}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{-}_{v(r)} \tag{11b}$$

for electrophilic attack.

By the finite difference method, using the electron densities of N_0, $N_0 + 1$, and $N_0 - 1$ electron systems, Fukui functions for the nucleophilic and electrophilic attack can be defined respectively as

$$f^{+}(r) \approx \rho_{N_o+1}(r) - \rho_{N_o}(r) \tag{12a}$$

$$f^{-}(r) \approx \rho_{N_o}(r) - \rho_{N_o-1}(r) \tag{12b}$$

and for radical attack

$$f^{o}(r) \approx \frac{1}{2}(\rho_{N_o+1}(r) - \rho_{N_o-1}(r)) \tag{12c}$$

To describe the site reactivity or site selectivity, Yang et al.[34] proposed the atom condensed Fukui function, based on the idea of electronic population around an atom in a molecule, similar to the procedure followed in the population analysis technique.[35] The condensed Fukui function for an atom k undergoing nucleophilic, electrophilic, or radical attack can be defined respectively as

$$f_k^{\,+} \approx q_k^{\,N_o+1} - q_k^{\,N_o} \tag{13a}$$

$$f_k^{\,-} \approx q_k^{\,N_o} - q_k^{\,N_o-1} \tag{13b}$$

$$f_k^{\,o} \approx \frac{1}{2}(q_k^{\,N_o+1} - q_k^{\,N_o-1}) \tag{13c}$$

where q_k values are electronic population of the kth atom of a particular species. The condensed local softness, s_k^{+} and s_k^{-}, is defined accordingly for nucleophilic and electrophilic attack, respectively.

In many cases, the interaction takes place not just with a single atom, but with a group of atoms. In such cases group softness and group FF can be defined as a sum of the local softness or FF of the group of atoms participating in the interaction. The group softness, s_g, is defined over the set of the atoms n_g and is written as

$$s_g = \sum_{k=1}^{n_g} s_k \tag{14}$$

This concept is very useful when reaction does not take place through a single atom, but through neighboring atoms in a cooperative manner, in other words, in cases where a group of atoms participate in bonding together. We can also define a concept of group FF, f_g, which is nothing but the sum of the FF of the atoms of the group. It is obvious that f_g is nothing but s_g/S, where S is the total softness of the system. For intramolecular reactivity, however, f_g and s_g will contain the same information. On the other hand, in comparing reactivity across different molecules, f_g and s_g will not necessarily give the same trend, since global softnesses of the systems vary.

Along the lines of electrophilic and nucleophilic condensed FF, we can define the electrophilic and nucleophilic condensed group softness and group FF, $s_g^{+/-}$ and $f_g^{+/-}$ etc. For the systems of metal clusters that are being studied, the Al_4 unit of atoms behaves as a superatom in acceptance of electrons and hence the concept of group softness or group FF will be extremely useful.

3. Computational Details

Geometry optimization of the metalloaromatic and antiaromatic clusters, viz., Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4, were performed at the MP2 level with all electrons, using the 6-31+G* basis set. The initial geometries of these clusters were obtained from the earlier experimental and theoretical work. The structural parameters of these clusters are in good agreement with the earlier work, which is discussed in the next section. The global minima of these clusters have been confirmed by frequency analysis. More detailed information on the geometrical parameters and the energetics of the clusters is given in the Supporting Information. Chemical potential, global hardness, and global softness are calculated from eqs 5, 6, and 7. The local reactivity parameters, such as condensed local softness and condensed FF, are obtained from the above equations by using Lowdin population analysis (LPA).[36] All the calculations in the present work have been performed by using GAMESS software.[37]

4. Results and Discussion

We begin this section with a brief discussion on the structural properties of the metalloaromatic and antiaromatic compounds, viz. ,Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4. Later, we discuss the use of group FF to analyze the reactivity in these systems.

I. Structure. The ground-state geometries of Al_4Na^-, Al_4Li_4, and Al_4Na_4 are shown in Figure 1. The ground-state geometry of Al_4Li^- also has a pyramidal structure similar to that of Al_4Na^- as shown in the Figure 1. For a more detailed study on the stability of these clusters, see the work by Shetty et al.[13] and Kuznetsov et al.[10] The ground state of Al_4Li^- and Al_4Na^- metalloaromatic clusters shows that the Al_4 unit has a square structure with the Al−Al bond lengths being 2.61 and 2.62 Å, respectively. However, the Al_4 unit of the metalloantiaromatic Al_4Li_4 and the Al_4Na_4 clusters has rectangular geometries (Figure 1b,c). The bond lengths of these clusters obtained from MP2 calculations in the present work are in good agreement with the earlier results.[1,13]

It is worth mentioning that in all the above-mentioned metalloaromatic and antiaromatic compounds, the Al atoms group to form one Al_4 unit in the whole cluster. This arrangement allows the Al_4 unit to form a superatom.[38] In a previous study, Shetty et al. have clarified the role of the Al_4 superatom in the Al_4Na_4 and $Al_4Na_3^-$ metalloantiaromatic compounds.[13] It should be noted that if there is no formation of the Al_4 superatom in the metalloaromatic and antiaromatic compounds, such as Al_4Li_2, Al_4Li_4, Al_4Na_4, etc., the charge transfer from the Li and Na atoms to the Al_4 unit would be difficult. Hence, the existence of aromaticity and antiaromaticity in these compounds is not possible. It is worth mentioning that the charge transfer from Li to Al at the Li−Al interface as discussed by Haskal et al.[19] would be due to the formation of the Al_n superatom. Detailed theoretical study of charge transfer and optical properties in the metalloantiaromatic compounds has been discussed by Datta et al.[39]

II. Reactivity. We now focus our discussion on the intercluster reactivity of the metalloaromatic and antiaromatic compounds. We investigate the trend of the nucleophilicity of the Al_4 unit in all four clusters, viz., Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4, using the group softness and FF.

a. Metalloaromatic Compounds: *Al_4Li^- and Al_4Na^-*. Table 1 presents the chemical potential, global hardness, and global softness values of Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4 clusters. We observe that the Al_4Na^- cluster has the highest global softness and hence would be the most reactive cluster. However, from the experimental point of view, we are only interested in the group reactivity of the Al atoms rather than the alkali atoms. The local reactivity parameters such as the condensed local

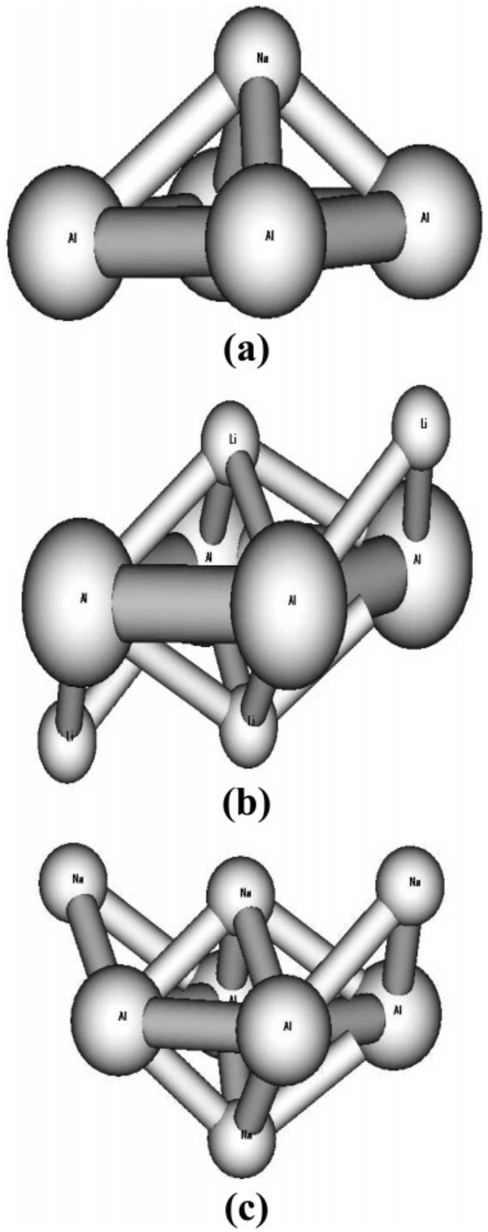

Figure 1. Optimized equilibrium geometries of (a) Al_4Na^-, (b) Al_4Li_4, and (c) Al_4Na_4 at the MP2 level with 6-31+G*.

TABLE 1: Chemical Potential, Global Hardness, and Global Softness of Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4 (values are in atomic units)

cluster	chemical potential, μ	global hardness, η	global softness, S
Al_4Na^-	−0.0055	0.0695	7.194
Al_4Li^-	−0.0055	0.0775	6.452
Al_4Na_4	−0.0565	0.0970	5.128
Al_4Li_4	−0.0845	0.1128	4.405

softness for the electrophilic (s^-) and the nucleophilic (s^+) attack, condensed FF for the electrophilic (f^-) and the nucleophilic (f^+) attack, and group softness (s_g^-) and the group FF (f_g^-) for the electrophilic attack of the Al_4 unit in the Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4 clusters are given in Table 2. Since we are only interested in the strength of the nucleophilicity (for the electrophilic attack or the strength of electron donation) of the Al_4 unit, we only discuss s_g^- and f_g^- for the electrophilic attack on the Al_4 unit, i.e., the nucleophilicity of the Al_4 unit.

As can be seen from Table 2, the condensed local softness and the condensed FF values for the electrophilic (s^-, f^-) and the nucleophilic attack (s^+, f^+) of all four Al atoms of the Al_4Li^- and Al_4Na^- clusters are identical. This is due to the electron delocalization in the Al_4 unit in both systems. Consequently, all four Al atoms in these systems have the same reactivity.

TABLE 2: Local Reactivity Parameters of Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4[a]

Al_4 unit	s^+	s^-	s_g^+	s_g^-	f^+	f^-	f_g^+	f_g^-
Al_4Li^- [b]	0.129	1.336	0.516	5.344	0.020	0.207	0.080	0.828
Al_4Na^- [b]	0.201	1.388	0.804	5.552	0.028	0.193	0.112	0.772
Al_4Li_4 [c]	0.366 0.344	0.542	1.420	2.168	0.083 0.078	0.123	0.322	0.492
Al_4Na_4 [c]	0.415 0.133	0.487	1.096	1.948	0.081 0.026	0.095	0.214	0.380

[a] Condensed local softness for nucleophilic (s^+) and electrophilic (s^-) attack and respective group softness s_g^+ and s_g^-. Condensed Fukui function for nucleophilic (f^+) and electrophilic (f^-) attack and respective group Fukui functions f_g^+ and f_g^-. [b] Values of condensed local softness and FF for nucleophilic and electrophilic attack for the four Al atoms in the Al_4 unit of the metal clusters Al_4Li^- and Al_4Na^- are the same. [c] Values of condensed local softness and FF for nucleophilic attack for two Al atoms are different than those of the other two Al atoms in the Al_4 unit of the metal clusters Al_4Li_4 and Al_4Na_4.

We can clearly see from Table 2 that the Al_4 unit of Al_4Li^- has a lower value of s_g^- than Al_4Na^-. Surprisingly, the trend of the group FF of these systems shows a different behavior (Table 2). This shows that the trend in the group softness and the group FF are not necessarily identical. However, from the definition of the group FF, we believe that the group FF is a more reliable indicator for the electrophilic or the nucleophilic attack than the group softness. Hence, only on the basis of the group FF can we say that in the metalloaromatic compounds the Al_4 unit of the Al_4Li^- cluster can act as a better electron donating system than the Al_4Na^- cluster.

b. Metalloantiaromatic Compounds: *Al_4Li_4 and Al_4Na_4*. The local reactivity parameters of the Al_4Li_4 and the Al_4Na_4 clusters are given in Table 2. Interestingly, the condensed local softness and FF of the metalloantiaromatic compounds show a different trend than the metalloaromatic compounds.

It can be seen from Table 2 that the values of the condensed local softness and the FF for the electrophilic attack of all four Al atoms of the Al_4Li_4 and Al_4Na_4 clusters are the same. Surprisingly, the values of the condensed local softness and condensed FF for the nucleophilic attack of two of the Al atoms are different from those of the other two Al atoms (Table 2). This shows that the ability to donate the electrons of all four Al atoms in both clusters is the same. However, the ability to accept the electrons of two Al atoms is different from that of the other two. The reason for this may be the electron localization along the shorter Al−Al bonds.

Unlike the metalloaromatic compounds, the group softness and the group FF results of the Al_4 unit of the metalloantiaromatic compounds show a similar trend. The Al_4 unit of the Al_4Li_4 cluster has a higher group softness and FF than that of the Al_4Na_4 cluster. If we compare the strength of nucleophilicity of the Al_4 unit only on the basis of group FF of all four clusters, viz., Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4, the trend is as follows: $Al_4Li^- > Al_4Na^- > Al_4Li_4 > Al_4Na_4$.

The above discussion demonstrates that the nucleophilicity of the Al atoms in the Al−Li systems is higher compared with that of Al−Na systems. However, the stoichiometry of the Al and Li also plays a crucial role in deciding the nucleophilicity of the Al cluster. From the present calculations, we can interpret that the strength of the nucleophilicity of the Al decides the work function of the Al−Li cathode. Hence, we can infer that the higher the nucleophilicity of the Al atoms, the lower is the work function of the Al atoms in the Al−Li cathode.

Curioni et al. proved in their study that the oxygen atoms of the Alq_3 molecule are the electron withdrawing groups (electrophiles).[21] Hence, from the present study one can interpret the metalloaromatic and antiaromatic systems to be molecular cathodes for injecting electrons where the Al can act as an electron injecting site in a single electroluminescent molecule, such as, Alq_3.

5. Conclusion

From the background of the experimental studies of the Al−Li cathodes, we propose to understand in this paper the enhanced efficiency of the electron injection due to the charge transfer from Li to Al and the clustering of the Al−Li atoms at the interface, based on theoretical calculations. We demonstrate the strength of the nucleophilicity of the Al atoms of various Al-based alkali clusters. For the first time, we have compared the intercluster reactivity of metalloaromatic and antiaromatic compounds using the local reactivity descriptors. The results suggest that the Al_4 unit in all four clusters, viz., Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4, acts as a nucleophile (electron donating groups). The group reactivity of the Al_4 unit, based on the local reactivity descriptors, suggests that the highest nucleophilicity of the Al_4 unit is in the Al_4Li^- cluster. Hence, we can say that the metalloaromatic (Al−Li) type of cluster formation, such as Al_4Li^-, at the interface of Al−Li alloys would be responsible for an efficient electron injection in the organic layer of OLED. Moreover, these types of clusters can be thought to be probable candidates for molecular cathodes. However, more experimental and theoretical work is needed to understand this issue.

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Supporting Information Available: Tables of *XYZ* coordinated and total energies of the metal clusters Al_4Li^-, Al_4Na^-, Al_4Li_4, and Al_4Na_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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