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Superatomic Molecules with Internal Electric Fields for Light Harvesting.

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Traditional p-n junctions used for photovoltaics require an interface where a light induced electron-hole pair is separated by an electric field. Developing alternate strategies for forming strong internal electric fields for electron-hole pair separation offers the possibility for better performance. We demonstrate that fusing two superatomic clusters with donor/acceptor ligands on opposite sides of the cluster leads to such a strong internal electric field. In two fused metal-chalcogenide $\text{Re}_8\text{S}_8\text{Cl}_2(\text{L})_4$ clusters with donor PMe_3 ligands and acceptor CO ligands on the opposite sides of the fused clusters, the electronic levels undergo shifts analogous to band bending in traditional p-n junctions. The fused cluster has a large dipole moment, and an optical spectrum that strongly absorbs excitations above the HOMO-LUMO gap of the fused clusters, but is optically very weak for the lowest energy excitations that can lead to electron-hole pair recombination. This is because the electron is localized on the CO portion of the fused cluster, while the electron-hole is localized on the PMe_3 side of the cluster. It is shown that the electronic states localized on each side of the cluster can be aligned/misaligned by applying voltage in different directions, offering diode like characteristics.

Introduction

The formation of an interface with an internal electric field can allow for the separation of electron-hole pairs as well as directed electrical transport.^{1–5} In a typical p-n junctions, n- and p- type semiconductors are joined together, and the chemical potential imbalance leads to a flow of charge across the junction boundary resulting in the formation of a depletion layer and an internal electric field.⁶ The internal electric field can separate electron-hole pairs or provide diode character as the width of the depletion layer can change with the direction of the applied voltage.^{7,8} In order to construct a p-n junction at the cluster level, one would need to join two clusters with different chemical potentials to produce such an internal electric field. However, in most fused clusters, where two superatomic clusters are strongly bound to each other, the clusters are identical.^{9,10} A dimer of two identical clusters will not generally exhibit a large internal electric field or dipole moment, and the binding of two different atom precise clusters requires exquisite chemical control.^{11–13} One promising candidate for such systems are metal chalcogenide clusters, as Roy, and co-workers have reported the formation of highly stable ligated metal-chalcogenide clusters including $\text{Co}_6\text{Se}_8(\text{PEt}_3)_6$, $\text{Cr}_6\text{Te}_8(\text{PEt}_3)_6$, $\text{Ni}_9\text{Te}_6(\text{PEt}_3)_8$. The clusters are composed of metal-chalcogenide cores with ligands such as triethylphosphine (PEt_3) attached to the metal sites.^{14–19} However, to create an internal electric field, the location of the

energy levels in the constituent units need to be controllable. In a recent work, we investigated this possibility in metal-chalcogenide clusters.^{20–24} The electronic donor or acceptor characteristics of these clusters can be controlled by attaching appropriate ligands.^{20,21} The electronic spectrum of metal-chalcogenide clusters can be raised or lowered by using donors (e.g. phosphine) or acceptors (e.g. CO) ligands where the phosphine raises the electronic spectra making the cluster a better donor, while the CO lowers the spectrum making the cluster a better acceptor.^{20,21} This can be done via raising or lowering the electronic spectra, without significant variation in the HOMO-LUMO (Highest Occupied Molecular Orbital, Lowest Unoccupied Molecular Orbital) gap. These predictions have since been confirmed by experiments and provide a unique possibility to tune donor or acceptor characteristics without changing the electron count.²⁵ Recent experiments by Nuckolls and co-workers have also shown that it is possible to make molecular dimers of metal-chalcogenide clusters with a precise control over the placement of ligands.¹⁰ These fused metal-chalcogenide clusters are an ideal system for creating p-n junctions in the cluster size regime, but how can an internal electric field be induced?

In this work, we demonstrate that large dipole moments in fused molecular clusters can be generated by joining identical metal-chalcogenide clusters and breaking the symmetry by ligating opposite units of the fused cluster with donor or acceptor ligands. Re_8S_8 is our first example because it has the largest HOMO-LUMO gap of the metal chalcogenide clusters, when it is in the +2 oxidation state, and it is known to be a semiconductor when assembled into materials.^{26–30} When the clusters are fused together, the interface is marked by bonds

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between the Re and S sites belonging to the two units. We then attach charge donating PMe_3 (Trimethylphosphine) ligands that make one side of the fused cluster a better donor, and charge accepting ligands, CO, making the other side of the fused cluster a better acceptor. The shift in the electronic levels in the composite superatomic molecule is reminiscent of the band bending found in conventional p- and n- junctions without the formation of the depletion layer. The difference in redox properties induced by the ligands leads to a large dipole moment. Investigations into the electric field required to counter the dipole indicates that the effect is equivalent to applying a voltage of 1.7 V across the cluster. We consider the fused cluster with separated donor-acceptor ligands to be a nano p-n junction. It is shown that the junction has an interesting transport characteristics in that the application of an electric field increases or lowers the barrier at the interface depending on the direction of the field suggesting that the nano unit has diode like characteristics. The absorption spectra reveals that the optical gap (the lowest energy excitation that readily absorbs light) of the fused clusters is significantly higher than the HOMO-LUMO gap of the fused clusters, and because the absorption at the HOMO-LUMO gap once the electron-hole pairs are separated is optically weak, this suggests that electron-hole pair recombination will be inhibited. The findings are fairly general and we also present results on Co_6S_8 based clusters to show that the concept may be extended to other dimeric superatom clusters.

Methods

The calculations were performed using the Amsterdam Density functional (ADF) set of codes.³¹ The first-principles methods used the PBE functional as proposed by Perdew, Burke, and Ernzerhof is for the exchange and correlation effects.³² The atomic wave functions are expressed in terms of Slater-type orbitals (STO) located at the atomic sites and the cluster wave functions are constructed from a linear combination of these atomic orbitals.³³ A TZ2P basis set and a large frozen electron core was used to ascertain completeness. The zero-order regular approximation (ZORA) is used to include scalar-relativistic effect.^{34,35} The electrical field calculations were performed by aligning an external electric field with the cluster, and the voltage was calculated by calculating the voltage difference of the terminal metal atoms. Optical absorptions were calculated using TD-DFT, and the lowest 500 excitations were calculated to simulate the spectra.

Results and discussion

Metal-chalcogenide clusters with large HOMO-LUMO Gaps

The first step towards developing such p-n junctions is the identification of clusters with well-defined valence and large HOMO-LUMO gaps. Such clusters, may be classified as superatoms, and are well positioned to maintain identity when integrated into assemblies.^{36,37} Within this context, metal chalcogenide clusters have recently received considerable

attention for the formation of functional solids with tuneable properties, including ferromagnetism, semiconductors with tuneable optical gaps and variable conductivity.^{10,14–19,38–40} An important advantages of this approach over traditional atomic solids is that the characteristics of the building blocks can be tuned pre-assembly and the building blocks are highly stable. Fig. 1 shows the ground state of $\text{Re}_6\text{S}_8\text{Cl}_2(\text{L})_4$ clusters, $\text{L}=\text{CO}$, or trimethyl phosphine (PMe_3). These clusters have HOMO-LUMO gaps of 1.49–2.25 eV depending on the ligand, and Fig. 2 shows the electronic levels of the cluster. $\text{Re}_6\text{S}_8(\text{L})_6$ clusters are well-known to be highly stable with 84 valence electrons, so the addition of 2 two Cl ligands is needed in order to close the electronic shell.

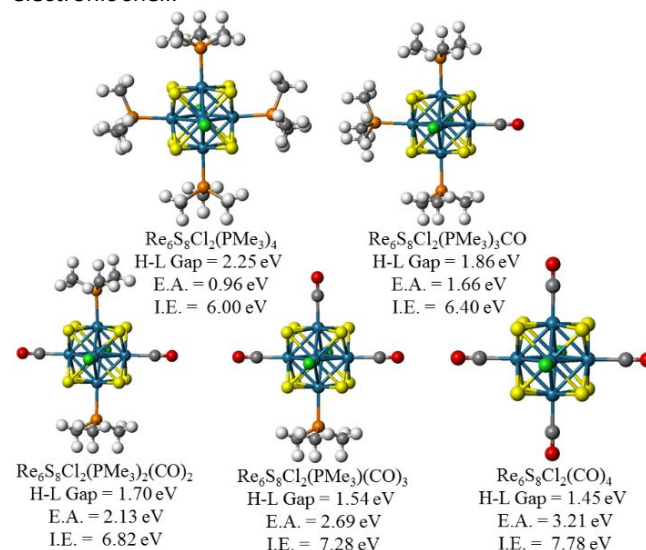


Figure 1. The structure, HOMO-LUMO gap, Adiabatic Electron Affinity (E.A.), and Adiabatic Ionization Energy, (I.E.), of $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_n(\text{CO})_m$.

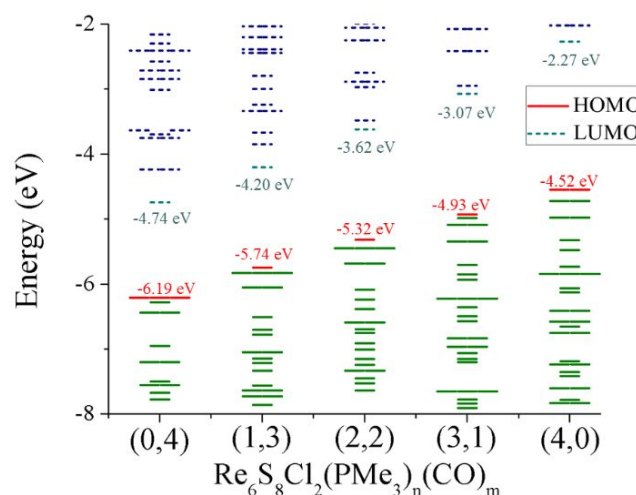


Figure 2. The electronic structure of $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_n(\text{CO})_m$.

Tuning the Electronic Spectrum of Metal-chalcogenide cluster.

By changing the ligand, superatomic clusters with closed electronic shells and large HOMO-LUMO gaps can be transformed into donors or acceptors while maintaining their electron shell closure. The electron affinity for $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_4$ is

3.21 eV, making it an excellent electron acceptor despite its large gap, and the cluster's electron affinity is much larger than the 0.96 eV electron affinity of $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_4$. $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_4$ has an ionization energy of 6.00 eV, much lower than the 7.78 eV of $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_4$, making the phosphine ligated cluster an significantly better electron donor. The unusual feature is that irrespective of the combination of ligands, the ligated species always have a closed shell electronic configuration with a high HOMO-LUMO gap, and that that the change in the electronic character is not associated with a change in the electron count. Instead, the donor/acceptor transformation is due to a shift in the electronic spectrum that can be rationalized as ligands forming a coulomb well that surrounds the cluster and may raise or lower the energy of the states depending on the donor-acceptor characteristics of the ligand. This can be clearly seen in Figure 2, in which the absolute HOMO and LUMO of the ligated clusters are graphed. The electronic structure of the ligated clusters is effectively isoelectronic with each other, but their donor/acceptor characteristics are drastically different. In recent works, these findings have been confirmed by experiments.²⁵

Cluster Fusion

Based on this concept that the ligand may transform a cluster from a donor to an acceptor, we fused two $\text{Re}_6\text{S}_8\text{Cl}_2(\text{L})_4$ clusters. We consider the case where the PMe_3 ligand transforms one cluster into a donor, and the other cluster is transformed into an acceptor by the addition of CO ligands. The superatoms bind with the Sulfur of one cluster binding the Re of the adjacent cluster. Hence, we decorated the stable $\text{Re}_6\text{S}_8\text{Cl}_2$ cluster with 3 CO and 3 PMe_3 ligands to form $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$ and $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ motifs. Figure 3 shows the structure of the three fused clusters or superatomic molecules with two $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ motifs, B) the mixed $\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3:\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$ cluster, and C) two $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$ clusters. The binding energies of the fused clusters are 1.67 eV, 1.80 eV, and 1.62 eV, respectively, showing that the fused clusters are reasonably stable. The enhanced binding energy of the fused clusters with mixed ligands is more stable due to the binding enhancement due to donor-acceptor pair forming.^{23,41–45} The HOMO-LUMO gap of the clusters are 2.00 eV, 1.11 eV, and 1.48 eV, showing that they all have a significant gap. The next question is whether the fusion of these superatomic clusters results in a strong internal electric field. The simplest way to test this is to find the dipole moment of the clusters. The dipole moment of the mixed cluster is 11.2 Debye, an extremely large dipole moment, while the moment of the all PMe_3 and CO clusters are 0.31 and 0.30 Debye. This result suggests that there is an extremely strong internal electric field in the mixed cluster that causes a redistribution of charge, and this result is consistent with our donor-acceptor hypothesis. Next, we investigate the optical spectra of the cluster, using Time Dependent-Density Functional Theory (TD-DFT). We have checked our results with a TD-DFT calculation that includes a perturbative spin-orbit coupling, and find no significant changes in the excitation energies.⁴⁶ We find that the optical

absorption of the mixed cluster is optically very weak for the HOMO-LUMO gap, and the optical gap is effectively 1.52 eV. This corresponds to the 8th lowest excitation, which is the first excitation with a non-negligible oscillator strength. The pure CO cluster has nearly the same optical gap of 1.50 eV, which corresponds to the lowest energy excited state, and the PMe_3 cluster has an optical gap of 2.03 eV. The results with the mixed cluster suggests that an excitation of the CO side of cluster may strongly absorb light, however the lower energy excitations that the cluster will decay to are optically weak which should inhibit electron-hole pair recombination.^{47,48}

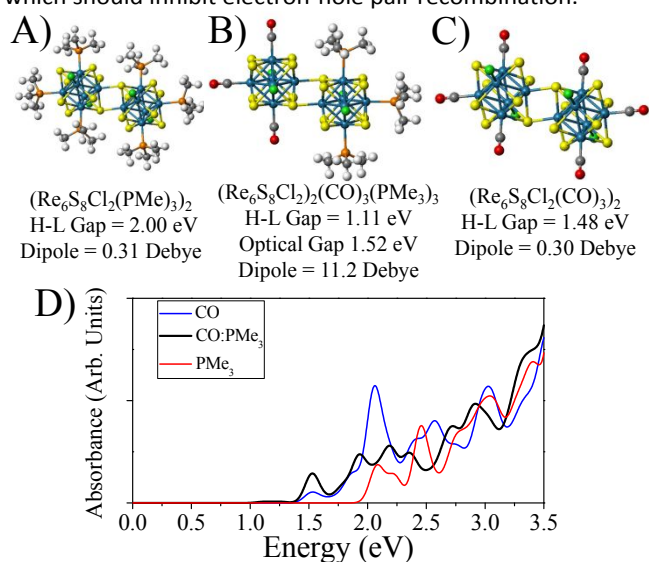


Figure 3. The structure, HOMO-LUMO gap, Optical Gap, and Dipole moment of A) ($\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$)₂, B) $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3:\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$, and C) ($\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$)₂. D) The calculated optical absorption spectra of ($\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$)₂, $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3:\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$, and ($\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3$)₂.

A Cluster p-n junction

We now want to determine if the combined donor-acceptor units are genuine superatomic models of p-n junctions, and whether they can separate electron-hole pairs. The combined superatomic molecule $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3:\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ is composed of an acceptor (CO) and donor (PMe_3) superatoms. The I.E. and E.A of 6.49 eV and 2.90 eV, which are in between the values of the clusters with all PMe_3 ligands, 5.86 eV, and 1.68 eV, and all CO ligands, 7.37 eV, and 3.54 eV. An analysis of the charge distribution indicates that there is a net charge flow of 0.14 e⁻ from the PMe_3 donor side to the CO acceptor. Next we look at the charge distribution of the anionic and cationic clusters. In the anionic cluster (Figure 4A), shows the excess charge is localized on the acceptor, CO side of the cluster, while in Figure 4B the hole is localized on the PMe_3 side of the cluster. This demonstrates that the electron-hole pair are well-separated on the different sides of the fused cluster. Next, we want to know if the superatomic molecule (Fig. 4C) has band bending at the interface, one of the hallmark characteristics of a p-n junction. Figure 4D shows the local density of states as a function of the position. The acceptor, CO, side of the cluster has effectively no density at the HOMO energy level, and the valence band energy is at -0.49 eV. The conduction band

energy of the CO side is at 1.12 eV, with the gap on the CO side of the cluster being effectively 1.61 eV. On the PMe_3 side of the cluster, the valence band is at 0 energy, and the conduction band is at 1.73 eV. Thus the valence band of the PMe_3 side is 0.49 eV higher than the CO side, and the conduction band is 0.61 eV higher in energy. It is intriguing that both side of the cluster have local density of states with gaps of 1.61 and 1.73 eV, but the states of PMe_3 side are raised with respect to the CO side, a clear analog of band bending. This gives the appearance of a reduction of overall band width, but is in fact due to band bending.

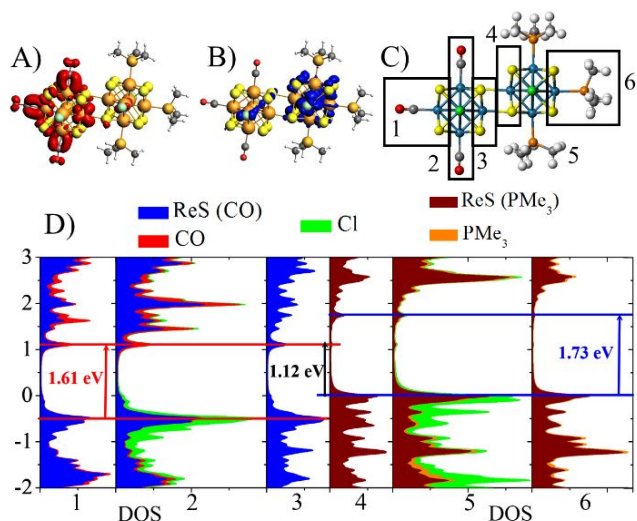


Figure 4. The structure of the A) Anionic, B) Cationic, and C) Neutral $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$. The isosurface indicates the excess charge, and electron hole. D) shows the density of states at different locations in the fused cluster. The position is indicated in part C.

Effect of an External Electric Field on the Fused Clusters

To examine the response of the electronic structure, an external field was applied to the mixed cluster, and the density of states and band energies are shown as a function of the voltage across the two terminal Re atoms. The field strength corresponds to 2.57×10^9 V/m for the 2.6 V calculation, which is similar in strength to the 10^9 V/m electric fields found under an STM tip.⁴⁹ Fig. 5 shows the density of states as a function of the field, and Figure S1 show the dipole moments, and Figure S2 shows the HOMO-LUMO gap and total energy as a function of the field. When the voltage across the terminal Re atoms is -1.55 V, the dipole moment approaches zero, and the HOMO-LUMO gap of the cluster increases to 1.47 eV. At a voltage of -1.55 V, the valence band of both sides of the cluster become aligned, causing this increase in HOMO-LUMO gap. On the other hand, if the electric field is aligned as positive towards the acceptor CO, and negative towards the donor PMe_3 , the electronic spectrum on the CO side of the fused cluster is lowered in energy versus the PMe_3 side. This leads to a reduction in the HOMO-LUMO gap, and the potential drop from the PMe_3 valence band to the CO valence band increases to 1.19 eV, versus the 0.49 eV at zero field. This field dependent shift indicates that the unit could be used a

rectifier in that it allows less resistance to the current in one direction while the resistance (barrier due to difference in HOMO) increases as the field is applied in the opposite direction. It is important to highlight that the current diode action is not due to any depletion layer as in conventional semiconductors but due to misalignment of states in the two regions.

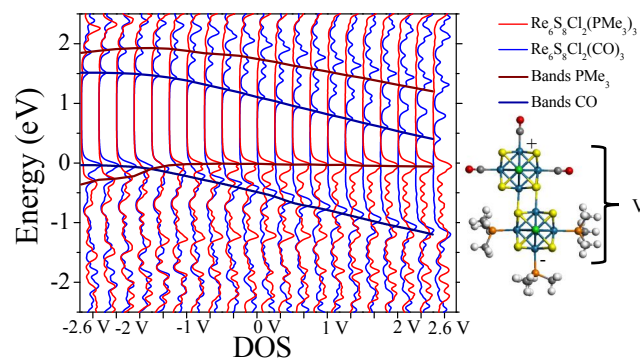


Figure 5. The density of states of the $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3\text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ cluster as a function of an electric field perpendicular to the cluster. The voltage across the terminal Re atoms are given, and the valence and conduction band energies of the CO and PMe_3 sides of the cluster are plotted.

To determine if this concept may be extended, we have examined the electronic structure of four fused $\text{Re}_6\text{S}_8\text{Cl}_2\text{L}_4$ clusters. In the tetramer cluster, the dipole moment has increased to 17.6 Debye. The HOMO-LUMO gap of the tetramer is 1.25 eV, the electron affinity increases from 2.86 eV for the dimer to 3.07 eV for the tetramer, and the ionization energy increases negligibly from 6.49 eV to 6.51 eV. The density of states reveals that the band bending across the cluster molecule has increased with the valence band on the far CO end of the cluster being 1.00 eV below the HOMO, while the energy of the valence band on the PMe_3 side is at the HOMO. Most of the band bending is at the junction, but there is a shift of 0.16 eV in the valence band across the outer and central CO ligated cluster, and a shift of 0.34 eV in the valence band across the outer and central PMe_3 cluster. The shifts in the valence band are approximately the same. The absorption spectra of the tetramer is shown in Figure S3, and reveals that again the strong absorption is across the HOMO-LUMO gap of the CO side of the tetramer, and the oscillator strengths of the lower energy excitations are quite weak. This is due to the excited electron being localized on the CO side of the molecule, while the electron hole is localized on the PMe_3 side of the cluster. The lack of overlap leads to a very small optical absorption. The separation and low oscillator strength suggests that electron-hole pair recombination will be inhibited. When we apply an electric field across the tetramer, we find that the bands are aligned when the voltage across the terminal Re atoms are 1.7 V, slightly higher than the 1.55 V of the dimer. This shows that the concept may be extended to longer wires, and may even be used to produce pnp or npn type junctions.

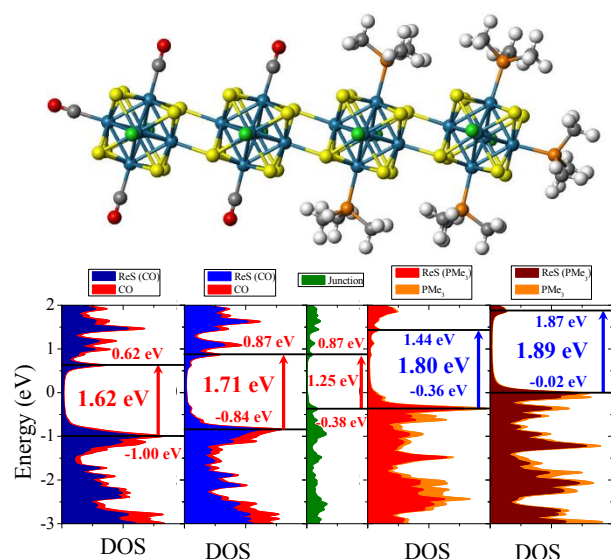


Figure 6. The density of states of the tetramer $\text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_3 : \text{Re}_6\text{S}_8\text{Cl}_2(\text{CO})_2 : \text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_2 : \text{Re}_6\text{S}_8\text{Cl}_2(\text{PMe}_3)_3$ cluster as a function of position.

In this work we have focused on metal-chalcogenide species based on Re_6S_8 cores. However, our findings are fairly general. To show this we investigated the $\text{Co}_6\text{S}_8(\text{CO})_5 : \text{Co}_6\text{S}_8(\text{PMe}_3)_5$ fused cluster. We find that the clusters bind by 2.45 eV, and that the cluster has a dipole moment of 18.0 Debye, even larger dipole than that for the Rhenium cluster. The cobalt cluster does not need Chlorine to close its electronic shell, so the dipole is larger. The HOMO-LUMO gap is only 0.29 eV with the frontier orbitals being localized in the p-n junction. The optical absorption is shown in Figure 7B, and there is a weak absorption corresponding to the excitation in the junction, however the absorption at the individual cluster's HOMO-LUMO gap is much stronger. The absorption here is larger than in the rhenium cluster, so it seems likely that the chance of electron-hole pair recombination will be larger in this cluster. In Figure 7C, we see the band bending in the $\text{Co}_6\text{S}_8(\text{CO})_5 : \text{Co}_6\text{S}_8(\text{PMe}_3)_5$ fused cluster. While the frontier orbitals are in the gap, the valence band in the CO side is found to be at -0.68 eV, while the valence band on the PMe_3 side is -0.21 eV. This shows that the use of donor/acceptor ligands on opposite sides of the cluster will induce a large internal electric field in different clusters. While the Cobalt cluster is unlikely to work for electron-hole pair excitation due to the presence of these defect states in the junction, the concept may be applied to other ligated clusters.

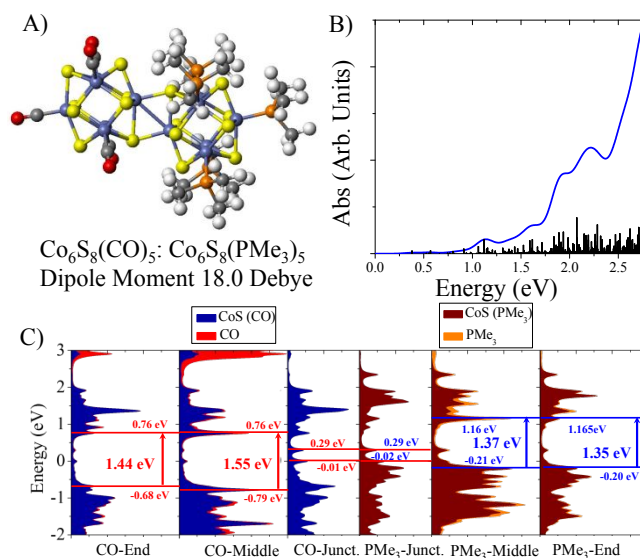


Figure 7. The structure of $\text{Co}_6\text{S}_8(\text{CO})_5 : \text{Co}_6\text{S}_8(\text{PMe}_3)_5$, the optical absorption spectra, and the density of states as a function of position.

Conclusions

The fusion of two metal-chalcogenide $\text{Re}_6\text{S}_8\text{Cl}_2(\text{L})_4$ clusters with charge donating ligands on one side and charge accepting ligands on the other side results in a cluster with a large dipole moment and internal electric field. This internal electric field may separate electron-hole pairs readily, because the electron is localized on the charge accepting CO side of the cluster and the hole is localized on the charge donating PMe_3 side of the cluster. Because of this strong internal electric field, the electron and hole are separated, inhibiting recombination. The fused clusters behave much like a cluster p-n junction, with the ligands acting as charge transfer dopants. An external electric field may realign the levels, and the response suggests that these fused clusters may behave much like a diode. The fused clusters may be extended into nanowires, opening the possibility of more complicated pnp and npn type junctions using this strategy. Further, this concept may be applied to other ligated clusters, although the presence of defect states in the cluster junction may prevent electron-hole separation, so the choice of cluster requires care for light harvesting. Furthermore, the synthesis of such an atom-precise material is quite challenging, however such fused clusters have been successfully synthesized.¹⁰ The use of multi-dentate ligands may be used to encapsulate one side of the cluster, which will greatly enhance binding. Another strategy would be to use a surface as a ligand, in which a surface such as a metal-chalcogenide or graphene surface may act as a donor or acceptor, and free ligands may act as the acceptor or donor. These results reveal an alternative strategy for forming and engineering internal electric fields at the scale of a single nanometer.

Conflicts of interest

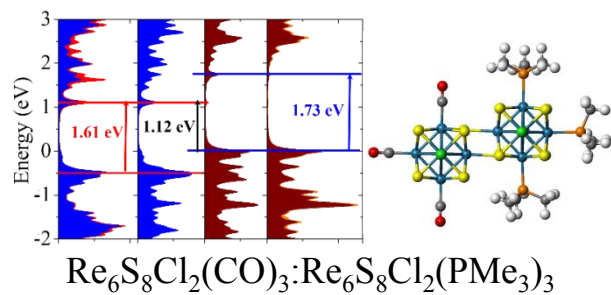
There are no conflicts to declare.

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Fusing two superatomic clusters with unbalanced donor-acceptor ligands leads to intense internal electric fields analogous to a pn junction.