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

Supplementary Information

Massive Dipoles across Metallic/Semiconductor Clusters Interface:

Towards Chemically Controlled Rectification

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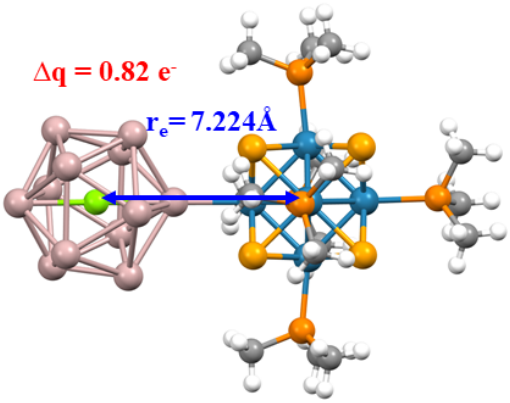
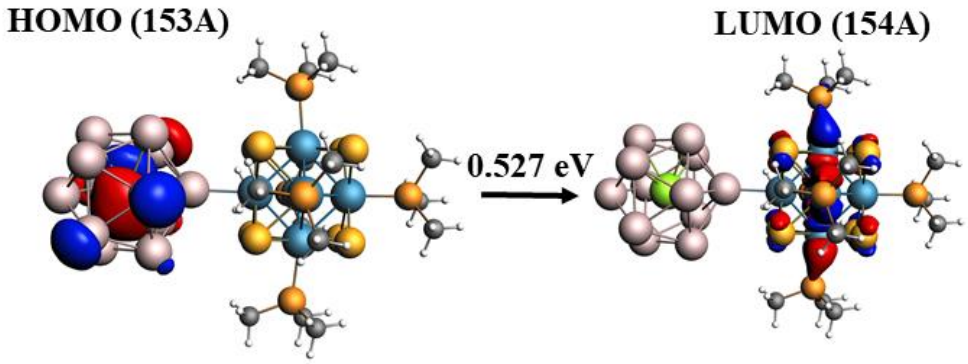


Dipole = Charge-transfer(**Δq**) x equilibrium distance between clusters(r_e)
= 0.82 e^- x 7.224Å
= 0.82 e^- x 7.224Å = 5.92 eÅ **[1D = 0.208194 eÅ]**
Dipole = 28.45 Debye

Supplementary Figure 1. The ground state structure of fused cluster $MgAl_{12}$-$Re_6Se_8(PMe_3)_5$ with the calculation of Dipole moment.



Supplementary Figure 2. The first optical transition near HL-gap. The states are seen separated in different regions between the transition states of $MgAl_{12}$-$Re_6Se_8(PMe_3)_5$.

Supplementary Table 1. Comparison of Hirshfeld and NPA charges on the fragments of the composite cluster, $MgAl_{12}$-$Re_6Se_8(PMe_3)_5$.

Comparison of Hirshfeld and NBO charges		
Fragments	**Hirshfeld-charge**	**NPA-charge**
$MgAl_{12}$	- 0.818	- 0.828
$Re_6Se_8(PMe_3)_5$	+ 0.819	+0.828

Supplementary Table 2. Comparison of relative energies for different multiplicities in clusters $MgAl_{12}$, $Re_6Se_8(PMe_3)_5$, and dimer $MgAl_{12}$-$Re_6Se_8(PMe_3)_5$.

Relative energy for Spin Different Multiplicities in eV			
Clusters	**1**	**3**	**5**
$MgAl_{12}$	0.05	0	0.86
$Re_6Se_8(PMe_3)_5$	0.03	0	1.77
$MgAl_{12}$-$Re_6Se_8(PMe_3)_5$	0	0.42	1.11

Cartesian-coordinates of optimized ground-state structures of $MgAl_{12}$, $Re_6Se_8(PMe_3)_5$, and $MgAl_{12}$-$Re_6Se_8(PMe_3)_5$ clusters.

$MgAl_{12}$

13
XYZ
Mg 0.06896 -0.004748 0.042142
Al 1.998714 -1.524073 -1.126572
Al 2.492967 -0.068914 1.291676
Al 0.125049 0.00494 -2.670147
Al -0.814346 -2.306788 -1.180787
Al 2.162824 1.367919 -1.118308
Al 0.623574 -2.382827 1.250097
Al 0.955763 2.298192 1.263012
Al 0.01532 -0.009732 2.755022
Al -2.357628 0.054006 -1.201376
Al -0.482588 2.37276 -1.168319
Al -2.019788 -1.379047 1.208529
Al -1.857423 1.51823 1.209846248

$Re_6Se_8(PMe_3)_5$

79
XYZ
Re 1.32999 1.802088 2.010946
Re 1.453267 1.96633 5.70374
Re 3.304668 2.168483 3.75294
Re 1.682745 -0.015692 3.90585
Re -0.509127 1.597384 3.908033
Re 1.106526 3.794327 3.75800
Se 3.52436 0.441214 5.657175
Se 2.986567 4.021776 5.537199
Se -0.62035 3.493691 5.6569
Se -0.070186 -0.110841 5.78217
Se 3.380831 0.286944 1.965853
Se 2.836879 3.838729 1.805099
Se -0.18069 -0.250814 2.124668
Se -0.716921 3.31644 1.971837
P 1.534906 2.196639 8.16493
P -2.932385 1.385036 3.898847
P 2.193026 -2.394368 3.87526
P 5.659705 2.682241 3.53182
P 0.923104 6.198391 3.582352

C	0.053945	7.049956	4.96647
C	2.499527	7.155336	3.51268
C	0.044275	6.866296	2.10914
C	1.176443	3.875635	8.82818
C	0.36765	1.158163	9.136342
C	3.14311	1.822998	8.976002
C	1.381647	-3.435535	5.160176
C	1.780677	-3.304022	2.329953
C	3.963043	-2.859	4.095887
H	0.044495	8.137926	4.81156
H	0.566121	6.814981	5.90792
H	-0.973927	6.673513	5.03403
H	2.298461	8.233022	3.43454
H	3.077896	6.821785	2.642163
H	3.083934	6.950659	4.41826
H	0.02682	7.964988	2.130802
H	-0.979897	6.474748	2.088681
H	0.558531	6.52111	1.203314
H	1.261855	3.88285	9.923672
H	0.163118	4.171304	8.53006
H	1.88724	4.589706	8.39417
H	3.077205	1.987513	10.06061
H	3.9161	2.473701	8.548428
H	3.42059	0.782191	8.770758
H	1.693445	-4.485348	5.067229
H	0.292903	-3.359726	5.050163
H	1.650566	-3.055117	6.153363
H	2.074991	-4.359837	2.411347
H	2.309872	-2.834511	1.491228
H	0.703348	-3.227913	2.139755
H	4.088776	-3.949281	4.038462
H	4.314764	-2.493816	5.068512
H	4.555363	-2.375285	3.30904
H	0.468554	1.360986	10.2118
H	0.570438	0.099449	8.93474
H	-0.657828	1.374542	8.81208
C	6.792468	1.919526	4.7691
C	6.459133	2.215867	1.94108
C	6.141093	4.458994	3.65691
C	-3.68671	0.42909	5.281391
C	-3.898726	2.953213	3.979028
C	-3.686379	0.578612	2.426232
H	7.832872	2.223838	4.58756
H	6.707839	0.827572	4.71059

H 6.486185 2.231139 5.77549
H 7.516559 2.515347 1.93591
H 5.927972 2.712427 1.11933
H 6.374948 1.132046 1.79643
H 7.224816 4.580374 3.51988
H 5.844779 4.844948 4.64004
H 5.604474 5.025084 2.88530
H -4.781347 0.405155 5.18625
H -3.408405 0.895757 6.23446
H -3.289443 -0.593168 5.273243
H -4.977693 2.746978 3.94715
H -3.616119 3.587132 3.12939
H -3.648342 3.483263 4.90618
H -4.781899 0.559815 2.51209
H -3.299482 -0.443434 2.334577
H -3.393319 1.135407 1.52729

$MgAl_{12}$-$Re_6Se_8(PMe_3)_5$

92
XYZ
Re 0.00168 0.03788 -0.97735
Re 0. 0. 2.7891
Re 1.87488 0.28846 0.89954
Re 0.27693 -1.85362 0.87514
Re -1.86727 -0.25063 0.89459
Re -0.26566 1.89279 0.91281
Se 2.06167 -1.54184 2.70523
Se 1.54948 2.06007 2.73851
Se -2.06363 1.54722 2.7336
Se -1.53306 -2.07107 2.6886
Se 2.04685 -1.48897 -0.97095
Se 1.5357 2.07793 -0.93036
Se -1.52473 -2.0084 -0.96125
Se -2.04668 1.56392 -0.92796
P -0.08217 0.07888 5.26264
P -4.3064 -0.53949 0.66246
P 0.69501 -4.27506 0.60963
P 4.29994 0.69621 0.6709
P -0.60144 4.32486 0.65804

C -2.12509 4.99894 1.43619
C 0.71693 5.39045 1.3672
C -0.72866 4.96397 -1.05875
C -0.12616 1.76304 5.9986
C -1.54916 -0.70438 6.04542
C 1.31036 -0.70028 6.17443
C -0.36031 -5.38996 1.62806
C 0.48686 -4.96899 -1.07941
C 2.39684 -4.83122 1.0424
H -2.20908 6.07811 1.2462
H -2.10137 4.8107 2.51563
H -2.997 4.48502 1.01405
H 0.48627 6.45053 1.19469
H 1.67251 5.14184 0.8879
H 0.80806 5.19898 2.44268
H -0.86208 6.05441 -1.04221
H -1.57933 4.49496 -1.56725
H 0.17901 4.70948 -1.6193
H -0.20159 1.70087 7.09366
H -0.99094 2.3077 5.59849
H 0.78426 2.30653 5.72007
H 1.16795 -0.59561 7.2591
H 2.25007 -0.22012 5.8776
H 1.37037 -1.76295 5.90968
H -0.09971 -6.44069 1.43866
H -1.41704 -5.22114 1.37236
H -0.22223 -5.15805 2.69384
H 0.7649 -6.03266 -1.08309
H 1.1186 -4.419 -1.7941
H -0.55936 -4.85822 -1.40037
H 2.49098 -5.91602 0.89359
H 2.61637 -4.57608 2.0903
H 3.11731 -4.31076 0.39602
H -1.51627 -0.57877 7.1368
H -1.57214 -1.77164 5.79308
H -2.45846 -0.23689 5.64696
C 5.39729 -0.47678 1.56455
C 4.98695 0.65467 -1.02957
C 4.88344 2.32751 1.28197
C -5.05139 -1.89569 1.65597
C -5.31998 0.91565 1.15123
C -4.94715 -0.89388 -1.02144
H 6.45176 -0.21956 1.39684
H 5.20634 -1.4949 1.20298

H 5.17287 -0.44531 2.63788
H 6.06024 0.88796 -1.00615
H 4.46369 1.38297 -1.66192
H 4.83418 -0.33913 -1.46681
H 5.96668 2.42856 1.12462
H 4.6511 2.42843 2.34821
H 4.35967 3.1215 0.73469
H -6.13649 -1.94264 1.48856
H -4.84553 -1.72963 2.72162
H -4.5939 -2.8497 1.36251
H -6.3875 0.704 0.99844
H -5.02833 1.7761 0.53515
H -5.13491 1.15955 2.20434
H -6.04406 -0.95263 -0.99974
H -4.53222 -1.84341 -1.38216
H -4.63225 -0.10112 -1.71357
Al -2.44044 -0.2159 -7.51091
Al -0.87534 -2.61847 -7.19848
Al 0.07106 -0.57907 -8.80811
Al -2.10482 -1.38151 -4.96994
Al -0.74101 1.98934 -7.77817
Al 1.99626 -1.80981 -7.26147
Mg -0.00098 -0.16828 -6.1946
Al -1.9721 1.47181 -5.27073
Al 0.68152 -2.44111 -4.86563
Al 1.96577 1.15354 -7.64905
Al -0.02055 0.0888 -3.59667
Al 0.73588 2.32895 -5.3764
Al 2.49999 -0.00997 -5.13826