Supporting Information

Single Vacancy Defected Endohedral Metallofullerene-Superhalogen Anions: Molecular Topology and Nonlinear Optical Responses of Na@C59[9-4]([8-5])-AlX_4 (X=Cl,Br) Systems

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Table S1. Optimized Cartesian coordinates (in Å) for Na@C59[9-4]-AlCl4 and Na@C59[9-4]-AlBr4 at the M06/LANL2DZ Level of Theory……..…….**S3**

Table S2. Optimized Cartesian coordinates (in Å) for Na@C59[8-5]-AlCl4 and Na@C59[8-5]-AlBr4 at the M06/LANL2DZ Level of Theory……..…….**S4**

Table S3. Optimized Cartesian coordinates (in Å) for Na@C60[6]-AlCl4 and Na@C59[6]-AlBr4 at the M06/LANL2DZ Level of Theory……..…….…….**S6**

Table S4. Optimized Cartesian coordinates (in Å) for Na@C60[5]-AlCl4 and Na@C59[5]-AlBr4 at the M06/LANL2DZ Level of Theory……..……..**S7**

Figure S1. Optimized geometrical structures of Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br) endohedral metallofullerene-superhalogen compounds……..**S9**

Figure S2. Simulated absorption spectra (green curves) and charge-transfer spectra (CTSs, colored curves) of **A**) Na@C59[9-4]-$AlCl_4$ and **B**) Na@C59[8-5]-$AlCl_4$.....**S10**

Figure S3. Contributions of molecular orbital (MO) transitions in **A**) Na@C59[9-4]-$AlCl_4$, and **B**) Na@C59[9-4]-$AlBr_4$, **C**) Na@C59[8-5]-$AlBr_4$ and **D**) Na@C59[8-5]-$AlCl_4$,The numbers outside and inside the parentheses denote the energy gaps of the orbital (eV) and the contribution of the electronic transition of the corresponding excitations (%), respectively.**S11**

Figure S4. Transition density matrix (TDM) of (A) Na@C59[9-4]-$AlBr_4$, (B) Na@C59[8-5]-$AlBr_4$, (C) Na@C59[9-4]-$AlCl_4$ and (D) Na@C59[8-5]-$AlCl_4$ compounds. (See Figure 1 for the isomer atomic number)…….**S12**

Figure S5. Total density of states (TDOS) map of **A**) Na@C59[9-4]-$AlCl_4$ and **B**) Na@C59[8-5]-$AlCl_4$ computed at the CAM-B3LYP/6-311G(d,p)/LANL2DZ level of theory……..**S13**

Figure S6. Simulated absorption spectra (green curves) and charge-transfer spectra (colored curves) of **A**) Na@C60[6]-$AlCl_4$, **B**) Na@C60[5]-$AlCl_4$, **C**) Na@C60[6]-$AlBr_4$, and **D**) Na@C60[5]-$AlBr_4$.....**S14**

Table S5. D, S_r, H, t Indices and Hole-Electron Coulomb Attraction Energies (E_{coul}) of the Selected Excited States of both the Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br) Isomers, Calculated at the CAM-B3LYP/6-311g(d,p)/LANL2DZ Level of Theory…….……**S15**

Figure. S7 Real space representations of hole and electron distribution of Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br). Green and blue regions denote the hole and electron distributions, respectively. The isovalues of hole and electron distributions are set to be 0.002 au……..……**S16**

Figure. S8 Scattering graphs between the reduced density gradient and sign (λ2) of **A**) Na@C59[8-5]-$AlBr_4$, **B**) Na@C59[9-4]-$AlBr_4$, **C**) Na@C59[9-4]-$AlCl_4$ and **D**) Na@C59[8-5]-$AlCl_4$ systems…….**S17**

Table S6. Polarizabilities (a.u) and (hyper)polarizabilities (a.u) in zero frequency limit and frequency-dependent fields…….**S18**

Figure. S9 Polarizabilities (α) responses of C60, Na@C60[6]-AlX_4, Na@C60[5]-AlX_4, Na@C59[9-4]-AlX_4 and Na@C59[8-5]-AlX_4 (X=Cl, Br) in zero frequency limit and frequency-dependent fields…….**S19**

Figure. S10 Variations of **A**) Poalrizability α (λ=1064.8 nm) and **B**) Hyperpolarizability β (λ=1064.8 and 589.08 nm) with the number of states……....**S20**

Table S1. Optimized Cartesian Coordinates (in Å) for Na@C59[9-4]-AlCl4 and Na@C59[9-4]-AlBr4 at the M06/LANL2DZ Level of Theory

Na@C59[9-4]-$AlCl_4$ (Charge=0 ; Spin multiplicity=1)				**Na@C59[9-4]-$AlBr_4$** (Charge=0 ; Spin multiplicity=1)			
Atom	***x***	***y***	***z***	***Atom***	***x***	***y***	***z***
C	0.20877500	2.54394500	2.20381300	**C**	-0.96521100	2.56511400	-2.14934400
C	0.66069500	3.40335200	1.11785000	**C**	-1.43764300	3.41491800	-1.06390900
C	-0.09053500	3.45960500	-0.05520100	**C**	-0.71316900	3.45199800	0.12580200
C	-1.34276200	2.69866400	-0.21997800	**C**	0.53150100	2.68368700	0.30980100
C	-1.62758300	1.72502500	0.73364200	**C**	0.84413700	1.72479700	-0.65378600
C	-0.90291900	1.72004400	1.99584400	**C**	0.14010800	1.73549900	-1.93016100
C	1.37883100	2.00593300	2.87965500	**C**	-2.12267800	2.04072200	-2.85651700
C	2.55928300	2.47721100	2.16057100	**C**	-3.31658200	2.50941700	-2.15805400
C	2.11204900	3.33179400	1.06493800	**C**	-2.88999100	3.34991500	-1.04370900
C	2.75874200	3.26974600	-0.17754700	**C**	-3.56376300	3.27689700	0.18381600
C	0.58072200	3.40924000	-1.34974600	**C**	-1.41136000	3.39661100	1.40556600
C	-1.63501700	2.53410600	-1.63029100	**C**	0.79477400	2.49848200	1.72143500
C	-2.06302700	-0.35150200	-0.79324200	**C**	1.24411200	-0.37342000	0.86066500
C	-2.00996600	0.33094100	0.42949100	**C**	1.21147000	0.32357600	-0.35742000
C	-1.67966800	-0.47096200	1.63815400	**C**	0.89773600	-0.46273200	-1.58085900
C	-0.94181300	0.38463800	2.54989500	**C**	0.18387200	0.40686600	-2.49824000
C	0.14862300	-0.10984000	3.27797400	**C**	-0.89361000	-0.07494700	-3.25478900
C	1.34976400	0.70812500	3.40382800	**C**	-2.08812100	0.74937600	-3.39618500
C	3.64790500	1.61758400	1.98224000	**C**	-4.41270200	1.65312600	-2.01319700
C	3.62252800	0.27347600	2.54255700	**C**	-4.38078800	0.31537200	-2.58844000
C	2.49935500	-0.16934000	3.24902800	**C**	-3.24494300	-0.12432300	-3.27622400
C	2.00784700	-1.53016500	3.06402800	**C**	-2.76344500	-1.48929800	-3.09690300
C	0.55618200	-1.49386800	3.10549100	**C**	-1.31087800	-1.45881500	-3.10754000
C	-0.19367100	-2.33665300	2.27904900	**C**	-0.58261500	-2.31449600	-2.27500900
C	-1.37267800	-1.83555600	1.59401500	**C**	0.58290800	-1.82634100	-1.55930700
C	-1.48508400	-2.53372800	0.33269800	**C**	0.66647100	-2.53963300	-0.30389000
C	-1.95015900	-1.81599700	-0.75213200	**C**	1.11425500	-1.83725300	0.79809800
C	-0.30767200	2.61317900	-2.21702500	**C**	-0.54384900	2.58840400	2.28289100
C	0.95988800	-2.06159000	-2.90390100	**C**	-1.84295900	-2.09219500	2.88383000
C	0.87634000	-0.71833800	-3.29160500	**C**	-1.76152900	-0.75357700	3.28794900
C	2.08239800	0.09015100	-3.27698500	**C**	-2.96420800	0.05953600	3.25811500
C	3.28389600	-0.41589200	-2.76593500	**C**	-4.15710700	-0.43572500	2.71695200
C	3.32020700	-1.76425100	-2.22457300	**C**	-4.18762500	-1.77768900	2.15965500
C	1.79429200	-3.39972800	-1.15513000	**C**	-2.64683100	-3.40818100	1.10413200
C	0.33863700	-3.44732700	-1.09338600	**C**	-1.19043500	-3.46154200	1.07223800
C	-0.16278200	-2.66473600	-2.21948500	**C**	-0.70910800	-2.69275100	2.21654600
C	-1.28521200	-1.87773800	-2.02740200	**C**	0.42058800	-1.90878400	2.05722900
C	-1.31491700	-0.42211300	-2.20640100	**C**	0.45504100	-0.45558800	2.25451200
C	-0.26979500	0.16527800	-2.93132300	**C**	-0.60382700	0.12942900	2.96272800
C	1.71020600	1.46502800	-3.03279600	**C**	-2.58225100	1.43537500	3.03846400
C	2.55962800	2.31717300	-2.31908200	**C**	-3.41398700	2.29940800	2.31807400

C	3.76201100	1.77352500	-1.70794600	**C**	-4.60509200	1.76753300	1.67527600
C	4.11718200	0.43751800	-1.92686600	**C**	-4.96962200	0.43051900	1.87097600
C	4.61747900	-0.37713900	-0.83085200	**C**	-5.44992800	-0.36947300	0.75519600
C	4.12530900	-1.73736100	-1.01592900	**C**	-4.96745100	-1.73368400	0.93488100
C	3.73845800	-2.50095500	0.09005700	**C**	-4.56051200	-2.48642700	-0.17144800
C	2.55156800	-3.34078700	0.02107000	**C**	-3.37886600	-3.33218100	-0.08711600
C	-0.30917600	-3.37999000	0.15654100	**C**	-0.51640700	-3.38285400	-0.16271100
C	0.48269500	-3.26949500	1.37624300	**C**	-1.28177400	-3.25455200	-1.39742000
C	1.88104600	-3.27508400	1.31508900	**C**	-2.68086800	-3.25460900	-1.36584300
C	2.65728900	-2.39576400	2.17785800	**C**	-3.43513700	-2.36206500	-2.23470000
C	3.81097200	-1.92512100	1.42542900	**C**	-4.60243300	-1.89508000	-1.50132000
C	4.28593400	-0.62141200	1.60461700	**C**	-5.06787600	-0.58717200	-1.67529500
C	4.70627800	0.16692300	0.45466400	**C**	-5.50927500	0.18979900	-0.52552000
C	4.31964700	1.55186300	0.68837800	**C**	-5.11257200	1.57576500	-0.73502300
C	3.87448500	2.34946100	-0.37062400	**C**	-4.68682800	2.35933000	0.34239200
C	0.26508400	1.54538700	-2.90069000	**C**	-1.13409500	1.51265600	2.93841100
C	1.96880000	3.27881000	-1.39857700	**C**	-2.80027100	3.26950100	1.42162300
C	2.18035900	-2.57020400	-2.29658500	**C**	-3.05290200	-2.58914500	2.24616500
Na	0.79824700	0.38495500	-0.12782700	**Na**	-1.60427900	0.37811800	0.14642000
Cl	-4.71990300	1.84894800	1.05000600	**Al**	4.95718800	0.00525600	-0.02130900
Cl	-7.82559100	0.15011700	-0.03605800	**Br**	4.18453700	-1.96976900	-1.20775700
Cl	-4.85613900	-1.76388200	1.15219900	**Br**	7.32908500	0.19748400	0.06711300
Cl	-4.72723800	-0.10130000	-2.04765600	**Br**	3.99245800	-0.12035400	2.23158500
Al	-5.62243500	0.03684300	0.03468700	**Br**	3.97279200	1.94686100	-1.16050800

Table S2. Optimized Cartesian Coordinates (in Å) for Na@C59[8-5]-AlCl4 and Na@C59[8-5]-AlBr4 at the M06/LANL2DZ Level of Theory

Na@C59[8-5]-$AlCl_4$ (Charge=-1 ; Spin multiplicity=2)				**Na@C59[8-5]-$AlBr_4$** (Charge=-1 ; Spin multiplicity=2)			
Atom	***x***	***y***	***z***	***Atom***	***x***	***y***	***z***
C	-0.19370600	1.49883600	2.98333300	**C**	-1.08781500	1.49533800	3.00590400
C	0.34935100	0.16313100	3.04865600	**C**	-0.55989100	0.15451600	3.08642500
C	1.33695400	-0.23047100	2.13689800	**C**	0.44595000	-0.25103500	2.19933000
C	1.76354300	0.65596000	1.03035100	**C**	0.90910200	0.62860600	1.10186600
C	1.42995500	2.01637800	1.15788300	**C**	0.58332800	1.99240900	1.21847400
C	0.34996300	2.40254600	2.06325400	**C**	-0.51345000	2.39155900	2.09742800
C	-1.62877600	1.42054400	3.19121200	**C**	-2.52825700	1.43197100	3.17922400
C	-1.97026500	0.02003000	3.42050000	**C**	-2.88913900	0.03540700	3.40219300
C	-0.74002500	-0.76180600	3.36966300	**C**	-1.66583300	-0.75878300	3.38227500
C	-0.75106400	-2.05195900	2.82648400	**C**	-1.67664300	-2.04987500	2.84138500
C	1.38976300	-1.60504200	1.68523000	**C**	0.49635200	-1.62714300	1.75193900
C	1.98812000	-0.23793500	-0.17378600	**C**	1.15630800	-0.27087500	-0.09508300
C	1.72434300	2.35092100	-1.24365700	**C**	0.94140600	2.31866200	-1.17398900
C	1.28370600	2.85024500	-0.04939700	**C**	0.47565900	2.82629800	0.00763000

C	0.00581300	3.50968600	0.01341200	**C**	-0.79592100	3.49935600	0.03818000
C	-0.55307700	3.29206500	1.33483800	**C**	-1.38906300	3.28939000	1.34595000
C	-1.93795500	3.19059700	1.50416700	**C**	-2.77853100	3.20185600	1.48154400
C	-2.49059300	2.24320500	2.45803800	**C**	-3.36342600	2.26161700	2.42340200
C	-3.15575700	-0.50448600	2.89305800	**C**	-4.06648600	-0.47814600	2.84683900
C	-4.03701900	0.34530000	2.09796400	**C**	-4.91970300	0.37880800	2.02931700
C	-3.70925700	1.68768200	1.88408800	**C**	-4.57334600	1.71742600	1.82111200
C	-3.90171500	2.28654400	0.56943400	**C**	-4.72780000	2.31567800	0.50112100
C	-2.81141000	3.21963600	0.33167700	**C**	-3.62292500	3.23735500	0.28824500
C	-2.26414300	3.35504600	-0.95328200	**C**	-3.04273500	3.36453300	-0.98325200
C	-0.82457700	3.49703300	-1.12414200	**C**	-1.59840500	3.49231100	-1.11951400
C	-0.42991300	2.68963000	-2.26838600	**C**	-1.18382800	2.67792200	-2.25207700
C	0.79245200	1.96881200	-2.22934100	**C**	0.02993200	1.94471600	-2.18228200
C	1.93023900	-1.57940900	0.35414300	**C**	1.06926900	-1.61030500	0.43447700
C	-0.71009700	-1.37586700	-3.14633100	**C**	-1.48425100	-1.38686500	-3.12951300
C	0.10124200	-2.26348400	-2.44197200	**C**	-0.69969100	-2.28187400	-2.40471800
C	-0.50993200	-3.24026800	-1.52802200	**C**	-1.34253700	-3.25021800	-1.50375700
C	-1.90270100	-3.25887900	-1.36707500	**C**	-2.73875300	-3.25407200	-1.37641000
C	-2.74644200	-2.37119800	-2.16132300	**C**	-3.55387400	-2.35933800	-2.19230000
C	-2.68164800	-0.10510000	-3.16736100	**C**	-3.44155500	-0.09613100	-3.20045900
C	-1.55279100	0.80093900	-3.34339100	**C**	-2.29950500	0.79803200	-3.35046100
C	-0.31552700	0.01729400	-3.23972400	**C**	-1.07336600	0.00215300	-3.21522200
C	0.80589800	0.53489800	-2.52728400	**C**	0.03572700	0.51030700	-2.47685200
C	1.55335200	-0.37207400	-1.61861200	**C**	0.75126800	-0.40315200	-1.54920300
C	1.31705000	-1.78179200	-1.83368800	**C**	0.50520100	-1.81056600	-1.76706600
C	0.37400000	-3.34402800	-0.35702700	**C**	-0.48835300	-3.36051800	-0.31130900
C	-0.19529600	-3.36934600	0.93851000	**C**	-1.08883600	-3.37680700	0.97025500
C	-1.63901200	-3.38330800	1.09325500	**C**	-2.53599700	-3.37595400	1.08999600
C	-2.48499600	-3.35758500	-0.03186700	**C**	-3.35411900	-3.34380000	-0.05529800
C	-3.68922700	-2.53989000	-0.00869700	**C**	-4.55023000	-2.51416400	-0.06302800
C	-3.86127700	-1.93924300	-1.32959200	**C**	-4.68422000	-1.91455000	-1.38876100
C	-4.37610100	-0.64444300	-1.44995600	**C**	-5.18273100	-0.61478200	-1.52394900
C	-3.78497900	0.28996600	-2.40000300	**C**	-4.55899700	0.31165700	-2.46089200
C	-1.62223800	2.09020300	-2.82401300	**C**	-2.36828900	2.08907000	-2.83529400
C	-2.76605900	2.50908700	-2.03095300	**C**	-3.52678400	2.52112400	-2.07110400
C	-3.82135200	1.61995400	-1.80733400	**C**	-4.59607000	1.64317100	-1.87158900
C	-4.40876300	1.50739400	-0.48157700	**C**	-5.21689400	1.53934900	-0.56045000
C	-4.75069300	0.11163700	-0.25831300	**C**	-5.57840400	0.14762600	-0.34311900
C	-4.57084800	-0.45843300	1.00749800	**C**	-5.43506400	-0.42175500	0.92772500
C	-4.03183300	-1.80676800	1.13387600	**C**	-4.91289100	-1.77513900	1.06950400
C	-3.15863600	-1.83423700	2.29960000	**C**	-4.06852000	-1.80906000	2.25587900
C	-1.98519800	-2.59706400	2.27654200	**C**	-2.90266600	-2.58375300	2.26289400
C	1.51603200	-2.51392700	-0.61566800	**C**	0.66750200	-2.54219500	-0.54353100
C	0.35572900	-2.50988500	1.99135600	**C**	-0.55468000	-2.52088700	2.03439900
C	-2.15401000	-1.45393700	-3.04128800	**C**	-2.93109700	-1.45005800	-3.05949700
Na	-0.71038400	-0.57949900	-0.04803800	**Na**	-1.55147300	-0.57664800	-0.04069800
Al	5.63472000	0.01352800	-0.00150100	**Al**	4.97647300	-0.00989000	0.00103500
Cl	4.83966100	-0.26460400	2.08947600	**Br**	4.10226900	-0.09439600	2.27353500

Cl	7.85629800	0.25309400	0.08786000	**Br**	7.38333700	0.21000200	0.08758800
Cl	4.73327200	1.89163000	-0.87382900	**Br**	4.06013900	1.95318000	-1.13263700
Cl	5.10437400	-1.74608400	-1.28604800	**Br**	4.36509700	-2.00841100	-1.22206900

Table S3. Optimized Cartesian Coordinates (in Å) for Na@C60[6]-$AlCl_4$ and Na@C60[6]-$AlBr_4$ at the M06/LANL2DZ Level of Theory

Na@C60[6]-$AlCl_4$ (Charge=0 ; Spin multiplicity=1)				**Na@C60[6]-$AlBr_4$** (Charge=0 ; Spin multiplicity=1)			
Atom	***x***	***y***	***z***	***Atom***	***x***	***y***	***z***
C	0.69985305	0.67979805	3.42913925	**C**	1.48661900	0.68538600	3.42767600
C	-0.38843303	1.41130210	2.79458220	**C**	0.39854600	1.41585800	2.79156600
C	-1.41910310	0.72335905	2.18427616	**C**	-0.63192300	0.72692500	2.18203900
C	-1.42032210	-0.73374805	2.17930816	**C**	-0.63314500	-0.73018800	2.17944500
C	-0.39083703	-1.42759510	2.78490320	**C**	0.39613600	-1.42305100	2.78651300
C	0.69867205	-0.70229705	3.42441025	**C**	1.48543400	-0.69671400	3.42519900
C	1.93633314	1.40618710	3.18025523	**C**	2.72318400	1.41136500	3.17802000
C	1.61325812	2.58712619	2.39191917	**C**	2.40037500	2.59101900	2.38765300
C	0.17735401	2.59162919	2.15437315	**C**	0.96455000	2.59513900	2.14962200
C	-0.32028002	3.02177122	0.93822007	**C**	0.46732200	3.02330000	0.93260400
C	-1.94189014	1.17805408	0.90362707	**C**	-1.15428200	1.17953300	0.90047700
C	-1.94382714	-1.17881108	0.89560107	**C**	-1.15622500	-1.17734100	0.89629100
C	-1.41592810	-2.29801417	0.28190102	**C**	-0.62812600	-2.29754500	0.28459200
C	-0.32539802	-3.02548222	0.91764007	**C**	0.46219000	-3.02397900	0.92187800
C	0.17294401	-2.60452919	2.13670215	**C**	0.96012800	-2.60104100	2.14041800
C	1.60884912	-2.60408718	2.37425917	**C**	2.39595400	-2.60021600	2.37845200
C	1.93393214	-1.42908810	3.17061523	**C**	2.72077600	-1.42392200	3.17300000
C	3.10884622	-0.73924405	2.93739021	**C**	3.89577000	-0.73446200	2.93904200
C	3.11007323	0.71595405	2.94233321	**C**	3.89700100	0.72074200	2.94161300
C	2.48121818	3.01784422	1.40609510	**C**	3.26866500	3.02012700	1.40141700
C	3.71658027	2.28928616	1.15452608	**C**	4.50410800	2.29115600	1.15144600
C	4.02330529	1.16885608	1.90262514	**C**	4.81058000	1.17194600	1.90147200
C	4.58663733	-0.00716700	1.25500209	**C**	5.37412300	-0.00513300	1.25595400
C	4.02131229	-1.18661509	1.89462114	**C**	4.80858100	-1.18353500	1.89730700
C	3.71266727	-2.30139616	1.13890408	**C**	4.50018400	-2.29954500	1.14330500
C	2.47607618	-3.02954722	1.38551810	**C**	3.26350800	-3.02729000	1.39069400
C	1.95186114	-3.47379325	0.10279401	**C**	2.73971800	-3.47362400	0.10852200
C	0.58827504	-3.47068925	-0.12492301	**C**	1.37620800	-3.47088700	-0.11965400
C	-2.25520316	0.00255200	0.10780601	**C**	-1.46733500	0.00273700	0.10646800
C	0.60928704	-1.40834910	-3.18151423	**C**	1.39824400	-1.41353200	-3.17959500
C	-0.56358204	-0.71751805	-2.93968021	**C**	0.22529700	-0.72230400	-2.93927700
C	-0.56234504	0.74050305	-2.93473621	**C**	0.22653800	0.73572300	-2.93670900
C	0.61171305	1.43096110	-3.17185823	**C**	1.40067700	1.42579000	-3.17456600
C	1.84791813	0.70189005	-3.42262625	**C**	2.63696300	0.69630800	-3.42373400

C	2.93332121	-1.41010010	-2.79146620	**C**	3.72214800	-1.41465400	-2.78877100
C	2.36766917	-2.58931519	-2.15177015	**C**	3.15627900	-2.59282300	-2.14734300
C	0.93159807	-2.58819319	-2.39356317	**C**	1.72028900	-2.59209100	-2.38961500
C	0.06363900	-3.01569422	-1.40540810	**C**	0.85200000	-3.01797800	-1.40105300
C	-1.17446208	-2.29280817	-1.15506008	**C**	-0.38618200	-2.29468100	-1.15229500
C	-1.47884411	-1.17021009	-1.90252014	**C**	-0.69031100	-1.17330200	-1.90168500
C	-1.47685111	1.18769909	-1.89450814	**C**	-0.68831300	1.18461700	-1.89751600
C	-1.17058409	2.30469817	-1.13944508	**C**	-0.38229300	2.30284400	-1.14417200
C	0.06877100	3.02713122	-1.38485010	**C**	0.85714600	3.02487200	-1.39034200
C	0.93602307	2.60486419	-2.37588817	**C**	1.72472600	2.60098800	-2.38040200
C	2.37209417	2.60190919	-2.13411715	**C**	3.16071700	2.59842300	-2.13814900
C	2.93575421	1.42610010	-2.78182820	**C**	3.72458800	1.42155800	-2.78375500
C	3.96862228	0.73284505	-2.17919216	**C**	4.75725300	0.72928300	-2.17964700
C	3.96737428	-0.72274505	-2.18413816	**C**	4.75600200	-0.72631300	-2.18222100
C	2.86506221	-3.02133522	-0.93730407	**C**	3.65326700	-3.02286500	-0.93200900
C	3.95330129	-2.29668017	-0.29695102	**C**	4.74129500	-2.29717000	-0.29247600
C	4.49083932	-1.17762409	-0.90408206	**C**	5.27903900	-1.17910700	-0.90125100
C	4.81564534	-0.00272600	-0.10781701	**C**	5.60358400	-0.00291300	-0.10679400
C	4.49284032	1.17811608	-0.89606506	**C**	5.28104600	1.17664300	-0.89707300
C	3.95721629	2.29393817	-0.28133402	**C**	4.74522100	2.29346700	-0.28433900
C	2.87021821	3.02480222	-0.91673507	**C**	3.65843700	3.02329800	-0.92129200
C	1.95776414	3.47168325	0.12643201	**C**	2.74563800	3.47188100	0.12084200
C	0.59416504	3.47249125	-0.10129401	**C**	1.38211500	3.47232200	-0.10733900
C	-2.03770915	0.00700000	-1.25378509	**C**	-1.24938800	0.00496500	-1.25505600
C	-1.41208610	2.30054117	0.29756202	**C**	-0.62427300	2.30103000	0.29275900
C	1.84672013	-0.67967805	-3.42730325	**C**	2.63576100	-0.68526600	-3.42615900
Na	0.83076906	0.00245200	-0.00963200	**Na**	1.61867600	0.00243600	-0.00994300
Al	-5.80751044	-0.00000300	-0.00874600	**Al**	-5.01960300	0.00000300	-0.01126100
Cl	-5.01335336	1.82110813	-1.04338307	**Br**	-4.17294000	1.93885800	-1.11669600
Cl	-8.04726060	-0.00134100	0.02471300	**Br**	-4.13678500	0.00042900	2.21577700
Cl	-4.98135336	-0.00299500	2.07333315	**Br**	-4.17091700	-1.93799800	-1.11677200
Cl	-5.01146436	-1.81687813	-1.04935808	**Br**	-7.36117000	-0.00133200	0.02294200

Table S4. Optimized Cartesian Coordinates (in Å) for Na@C60[5]-$AlCl_4$ and Na@C60[5]-$AlBr_4$ at the M06/LANL2DZ Level of Theory

Na@C60[5]-$AlCl_4$ (Charge=0 ; Spin multiplicity=1)				**Na@C60[5]-$AlBr_4$** (Charge=0 ; Spin multiplicity=1)			
Atom	***x***	***y***	***z***	***Atom***	***x***	***y***	***z***
C	0.41297403	1.60024011	2.66693619	**C**	-0.43701100	1.76451500	2.55910000
C	1.21438309	0.40422103	2.45703618	**C**	0.36215800	0.55601100	2.42635600
C	1.97634714	0.26653702	1.29634009	**C**	1.12377000	0.34276600	1.27690600
C	1.96847214	1.32063209	0.29438402	**C**	1.11777100	1.33045400	0.20941900
C	1.19916609	2.46745318	0.49356504	**C**	0.35061200	2.48911500	0.33462200
C	0.40534803	2.61093219	1.70300712	**C**	-0.44283900	2.71132900	1.53234500

C	-0.82832806	1.20186509	3.30960424	**C**	-1.67899800	1.41047900	3.22594500
C	-0.79413506	-0.24024502	3.50177625	**C**	-1.64746800	-0.01640200	3.51019700
C	0.46860103	-0.73378805	2.97548121	**C**	-0.38569400	-0.54502300	3.01668000
C	0.52013604	-1.96446914	2.31462017	**C**	-0.33649900	-1.81564200	2.43609800
C	2.03296415	-1.01485608	0.60585504	**C**	1.17795100	-0.98037000	0.67001300
C	2.01311415	0.69294905	-1.01726608	**C**	1.16114000	0.61987300	-1.05928000
C	1.28765809	1.23881909	-2.07591015	**C**	0.43661200	1.09808200	-2.15077600
C	0.48587303	2.43653517	-1.87042814	**C**	-0.36293000	2.30799700	-2.02255000
C	0.44163303	3.03601922	-0.61067204	**C**	-0.40595400	2.98711000	-0.80382900
C	-0.82059006	3.52786825	-0.08398501	**C**	-1.66721800	3.51406500	-0.30981300
C	-0.84338706	3.26486923	1.34640510	**C**	-1.69038700	3.34337300	1.13449700
C	-2.03501415	2.88480521	1.96716014	**C**	-2.88266700	3.00611200	1.77830100
C	-2.02736514	1.83096913	2.96856221	**C**	-2.87689300	2.01864600	2.84521900
C	-1.96018714	-0.99377207	3.34646124	**C**	-2.81493000	-0.77616900	3.40347700
C	-3.20874423	-0.33759802	2.99064522	**C**	-4.06229500	-0.14184200	3.00627000
C	-3.24021024	1.04564707	2.80406520	**C**	-4.09120800	1.22664800	2.73137300
C	-3.99758729	1.61483112	1.70063812	**C**	-4.84761700	1.72531100	1.59369000
C	-3.25216623	2.75092520	1.18298509	**C**	-4.10012900	2.82448500	1.00427900
C	-3.23045023	3.00445921	-0.18952701	**C**	-4.07805500	2.98944500	-0.38166500
C	-1.99003014	3.40159525	-0.83613306	**C**	-2.83695200	3.34199500	-1.05236000
C	-1.94514414	2.77557920	-2.14710515	**C**	-2.79333600	2.63312000	-2.32048900
C	-0.73208305	2.30176416	-2.65213619	**C**	-1.58119800	2.12564100	-2.79405200
C	2.05693315	-0.75052705	-0.82784106	**C**	1.20229300	-0.80856500	-0.77768100
C	-1.81322713	-1.17127509	-3.31194924	**C**	-2.66884500	-1.38054400	-3.22984200
C	-0.61333404	-1.80208213	-2.97073621	**C**	-1.47009700	-1.99040200	-2.84883600
C	-0.60541304	-2.85823321	-1.96835314	**C**	-1.46405600	-2.98011500	-1.78079100
C	-1.79866113	-3.23800723	-1.34661609	**C**	-2.65795600	-3.31702100	-1.13602500
C	-3.04691422	-2.58079418	-1.70247712	**C**	-3.90501600	-2.68166100	-1.53334400
C	-3.85572628	-0.37284803	-2.45780018	**C**	-4.70978700	-0.52519400	-2.42872600
C	-3.11124323	0.76325805	-2.97625322	**C**	-3.96323800	0.57394200	-3.01893600
C	-1.84886713	0.26974702	-3.50332425	**C**	-2.70182400	0.04530400	-3.51322900
C	-0.68342305	1.02232007	-3.34334724	**C**	-1.53497100	0.80441900	-3.40179500
C	0.56512804	0.36624803	-2.98857221	**C**	-0.28761200	0.17012700	-3.00563400
C	0.60129904	-1.01902607	-2.80755020	**C**	-0.25399900	-1.20075300	-2.73615300
C	0.61693705	-2.72920820	-1.18617509	**C**	-0.24140400	-2.80347200	-1.00845000
C	0.59746804	-2.98616121	0.19087901	**C**	-0.26123800	-2.97155700	0.38224600
C	-0.64910305	-3.37694424	0.83722106	**C**	-1.50848000	-3.31777200	1.05226900
C	-1.82130713	-3.50119325	0.08413201	**C**	-2.68097400	-3.48787700	0.30865400
C	-3.08398622	-3.00684222	0.61139604	**C**	-3.94268900	-2.95838700	0.80308500
C	-3.84152028	-2.43904018	-0.49288104	**C**	-4.69925800	-2.46115800	-0.33535700
C	-4.61004933	-1.29070009	-0.29372402	**C**	-5.46563700	-1.30098400	-0.21027500
C	-4.61809833	-0.23686902	-1.29616109	**C**	-5.47181100	-0.31358900	-1.27822600
C	-3.15773123	1.98967514	-2.31132017	**C**	-4.00739400	1.84055800	-2.43401600
C	-3.95170329	2.13099515	-1.10111008	**C**	-4.80100300	2.06066600	-1.23538900
C	-4.66769733	1.04069408	-0.60420704	**C**	-5.51898000	1.00580500	-0.66962000
C	-4.69089534	0.77724205	0.82541106	**C**	-5.54255100	0.83461200	0.77394800
C	-4.65531333	-0.66381505	1.01762207	**C**	-5.50962900	-0.59121700	1.05817200
C	-3.93031328	-1.20984809	2.07843715	**C**	-4.78555800	-1.06944900	2.15184400

C	-3.12796523	-2.40560617	1.87100814	**C**	-3.98544900	-2.27753600	2.02155000
C	-1.90976214	-2.27132616	2.65433719	**C**	-2.76693400	-2.09556700	2.79470100
C	-0.69528605	-2.74648620	2.14902316	**C**	-1.55338400	-2.60440800	2.32094200
C	1.36086510	-1.58926511	-1.70362312	**C**	0.50459700	-1.70044000	-1.59790400
C	1.32115710	-2.11054815	1.10438608	**C**	0.46415100	-2.04051400	1.23775200
C	-3.05368222	-1.56874211	-2.66477219	**C**	-3.90998300	-1.73338800	-2.55855600
Al	6.01094644	0.01454500	-0.00127900	**Al**	5.27999500	0.01034700	-0.00229800
Cl	5.23021938	-1.09477608	-1.71348512	**Na**	-1.47252400	-0.52904100	0.02895700
Cl	5.14668837	-0.89362507	1.79176613	**Br**	4.42764300	2.22517300	-0.28539300
Cl	5.22879338	2.04813615	-0.12964001	**Br**	4.42339400	-1.31940100	-1.79397400
Cl	8.15082260	-0.02182700	0.05305500	**Br**	4.33420600	-0.85233200	2.01596100
Na	-0.61836904	-0.52827204	-0.00515700	**Br**	7.66880600	-0.03072400	0.06092700

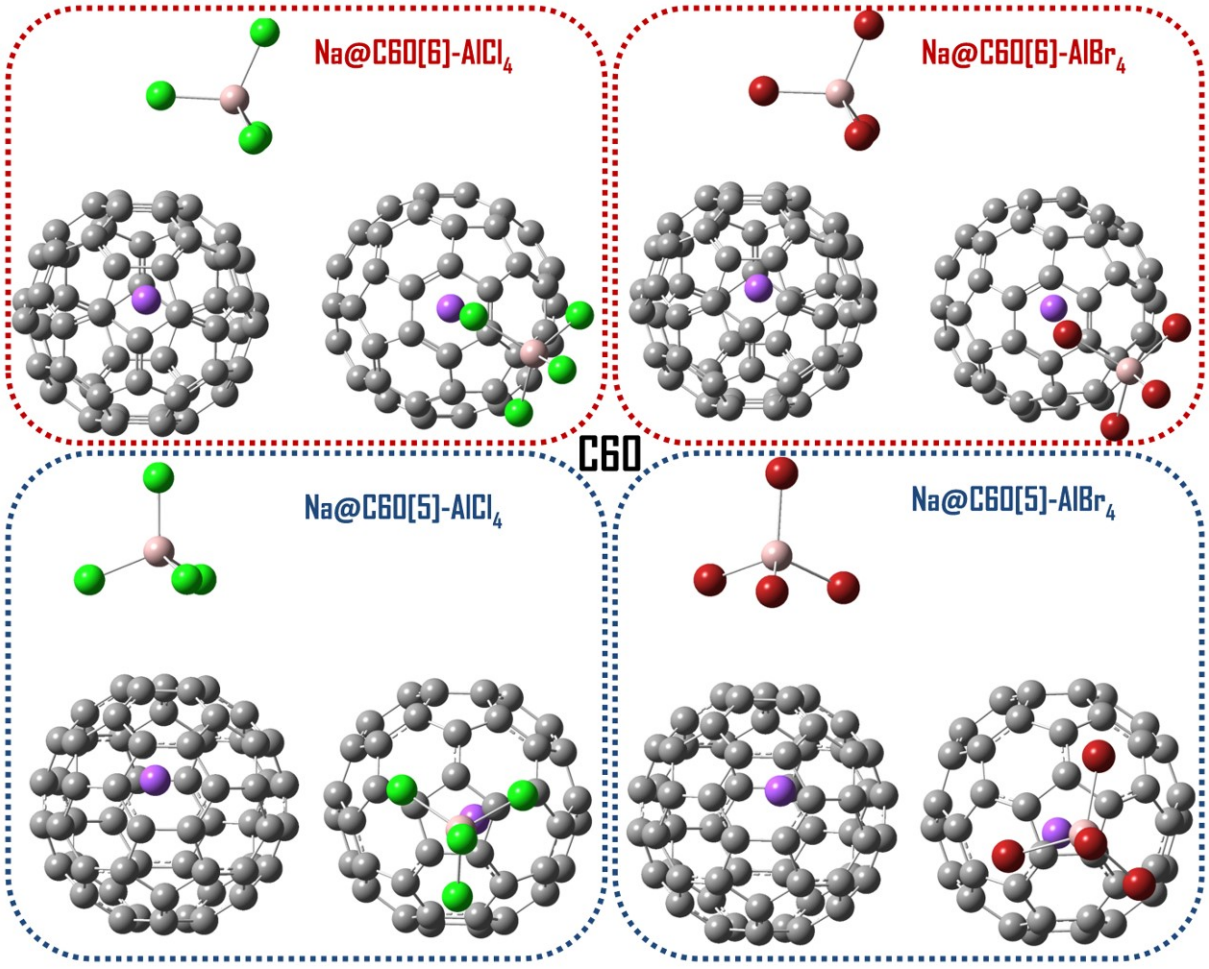

Figure S1. Optimized geometrical structures of Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br) endohedral metallofullerene-superhalogen compounds.

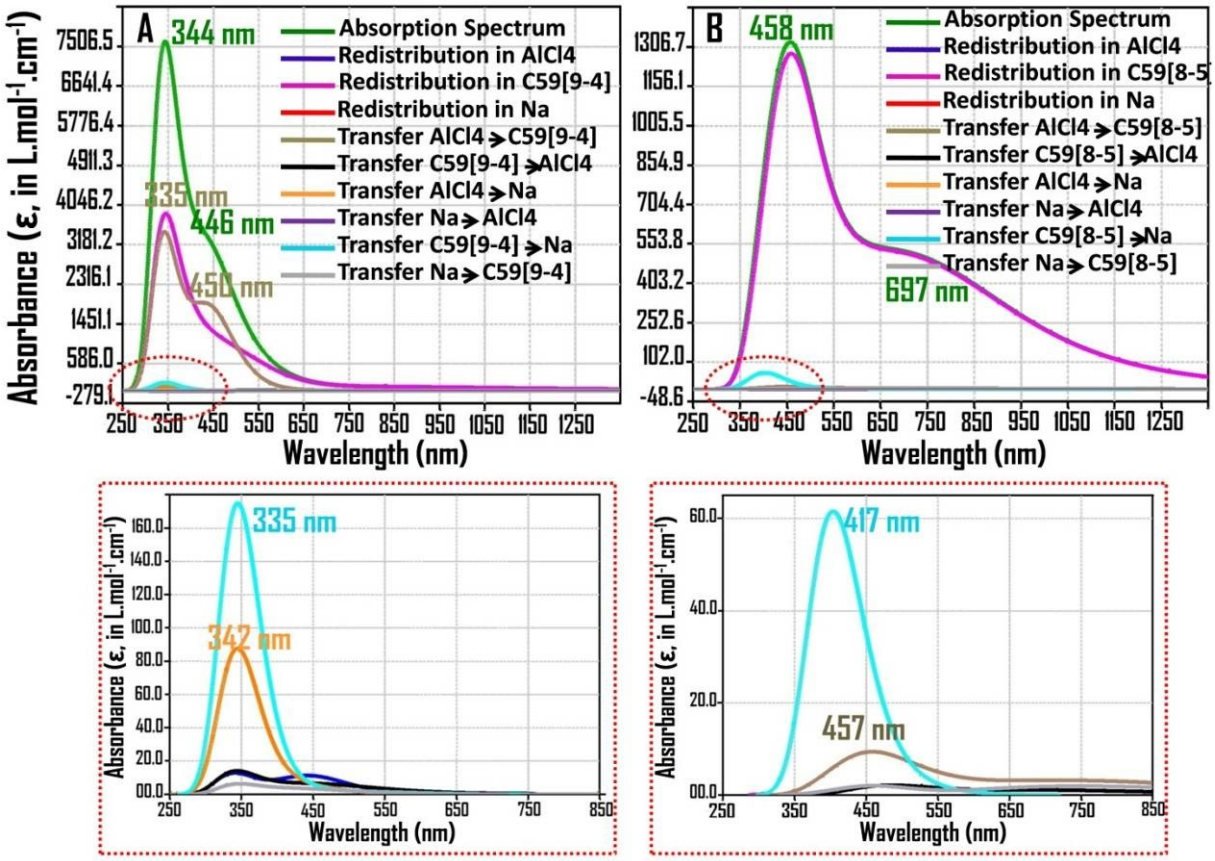

Figure S2. Simulated absorption spectra (green curves) and charge-transfer spectra (CTSs, colored curves) of **A**) Na@C59[9-4]-$AlCl_4$ and **B**) Na@C59[8-5]-$AlCl_4$.

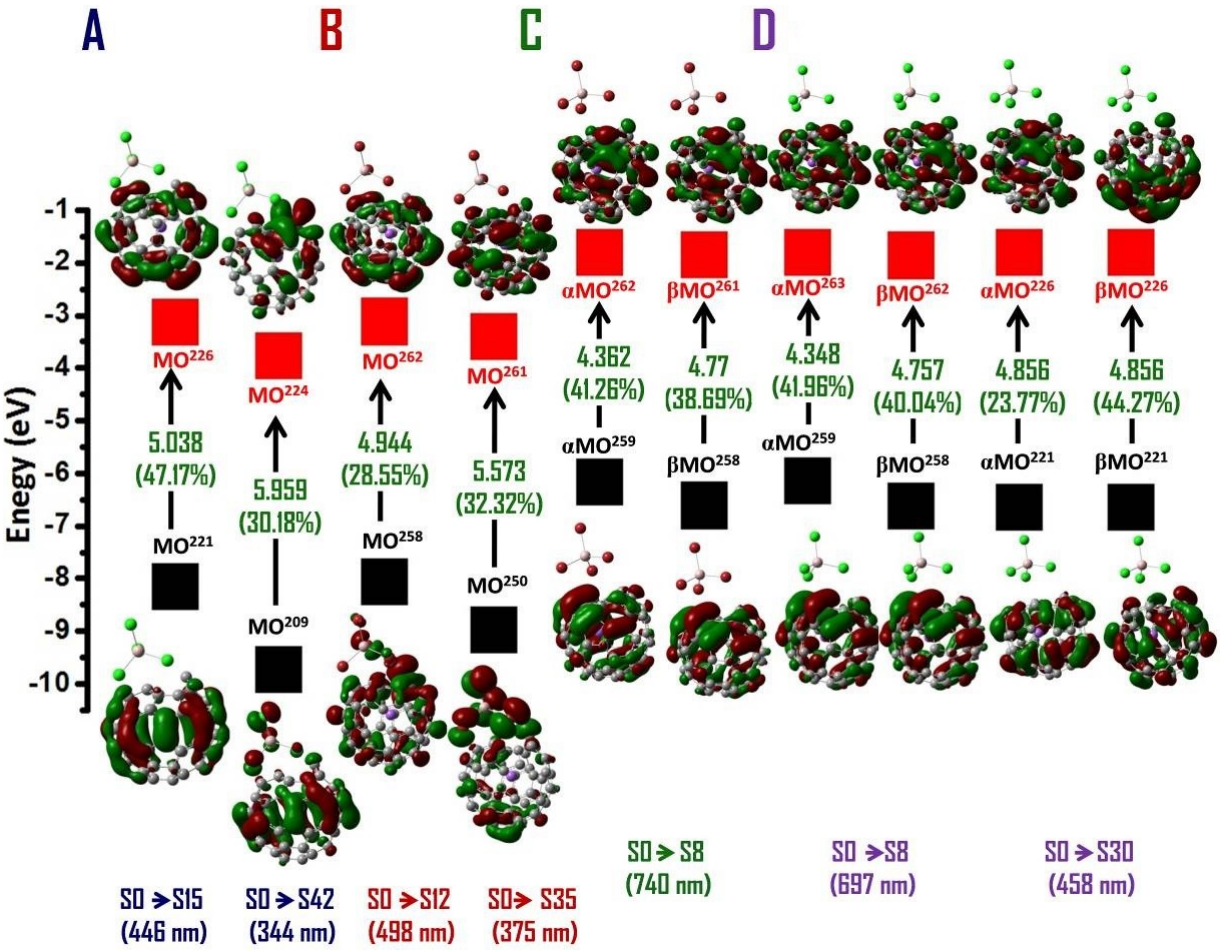

Figure S3. Contributions of molecular orbital (MO) transitions in **A**) Na@C59[9-4]-$AlCl_4$, and **B**) Na@C59[9-4]-$AlBr_4$, **C**) Na@C59[8-5]-$AlBr_4$ and **D**) Na@C59[8-5]-$AlCl_4$.The numbers outside and inside the parentheses denote the energy gaps of the orbital (eV) and the contribution of the electronic transition of the corresponding excitations (%), respectively.

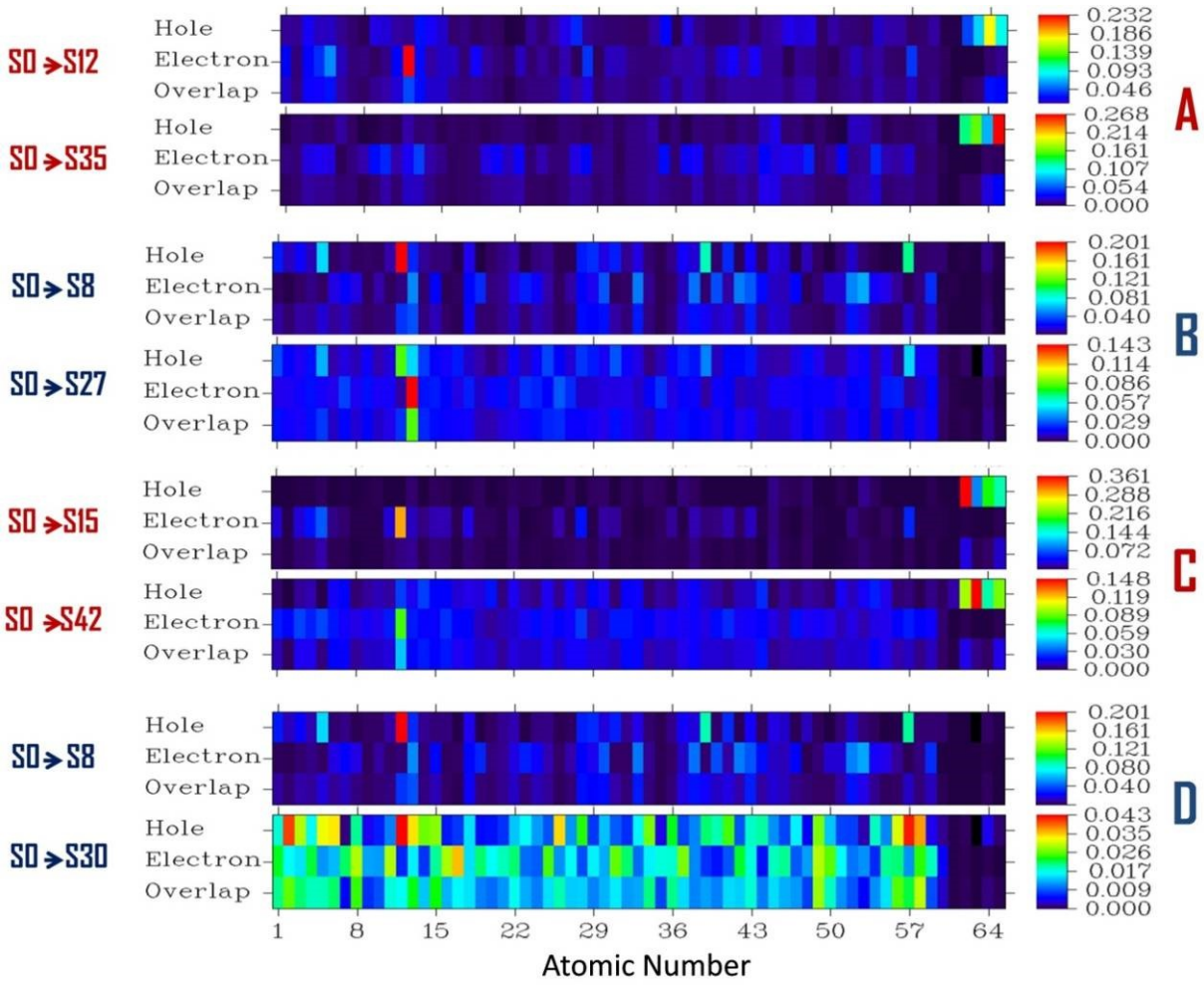

Figure S4. Transition density matrix (TDM) of **A**) Na@C59[9-4]-$AlBr_4$, **B**) Na@C59[8-5]-$AlBr_4$, **C**) Na@C59[9-4]-$AlCl_4$ and **D**) Na@C59[8-5]-$AlCl_4$ compounds. (See Figure 1 for the isomer atomic number).

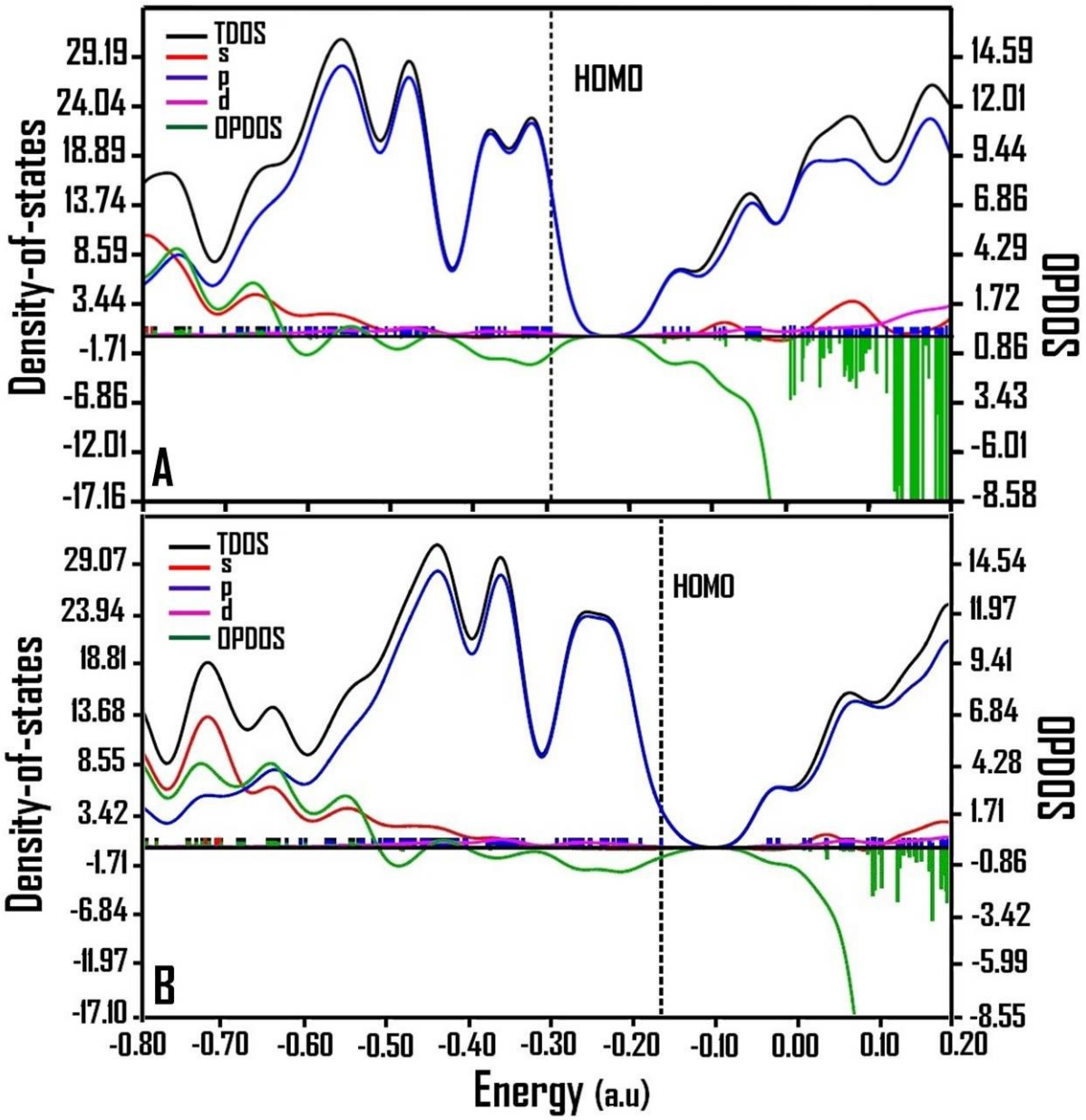

Figure S5. Total density of states (TDOS) map of **A**) Na@C59[9-4]-$AlCl_4$ and **B**) Na@C59[8-5]-$AlCl_4$ computed at the CAM-B3LYP/6-311G(d,p)/LANL2DZ level of theory.

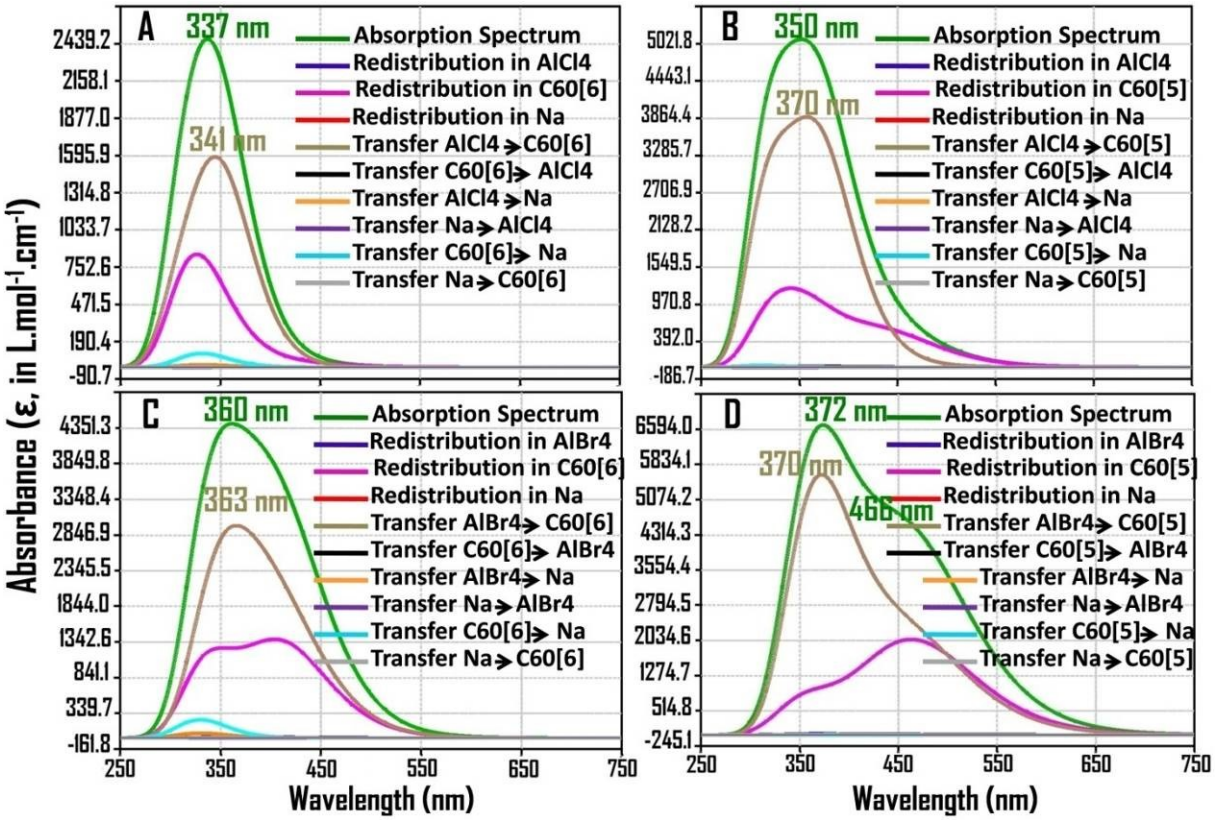

Figure S6. Simulated absorption spectra (green curves) and charge-transfer spectra (colored curves) of **A**) Na@C60[6]-$AlCl_4$, **B**) Na@C60[5]-$AlCl_4$, **C**) Na@C60[6]-$AlBr_4$, and **D**) Na@C60[5]-$AlBr_4$.

Table S5. *D*, S_r, *H*, *t* Indices and Hole-Electron Coulomb Attraction Energies (E_{coul}) of the Selected Excited States of both the Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br) Isomers, Calculated at the CAM-B3LYP/6-311g(d,p)/LANL2DZ Level of Theory.

States	***D*(Å)**	S_r	***H*(Å)**	***t*(Å)**	E_{coul}**(eV)**
			Na@C60[6]-$AlBr_4$		
S0 → S1[a]	0.663	0.860	3.949	-1.981	3.603
S0 → S21	1.802	0.786	4.260	-1.047	3.235
S0 → S37	5.809	0.404	3.933	2.958	2.602
			Na@C60[6]-$AlCl_4$		
S0 → S1[a]	0.428	0.876	3.878	-2.104	3.666
S0 → S22	6.010	0.429	3.639	3.316	2.488
S0 → S27	1.654	0.832	4.313	-1.199	3.218
			Na@C60[5]-$AlBr_4$		
S0 → S1[a]	2.182	0.744	4.288	-0.895	3.225
S0 → S11	4.806	0.438	3.896	2.112	2.796
S0 → S37	5.670	0.372	3.994	2.836	2.598
			Na@C60[5]-$AlCl_4$		
S0 → S1[a]	0.660	0.797	3.964	-1.793	3.561
S0 → S22	5.552	0.384	3.916	2.724	2.668
S0 → S45	5.783	0.386	3.781	3.319	2.489

[a] For comparison, the different indices are calculated for the first excited state (S1).

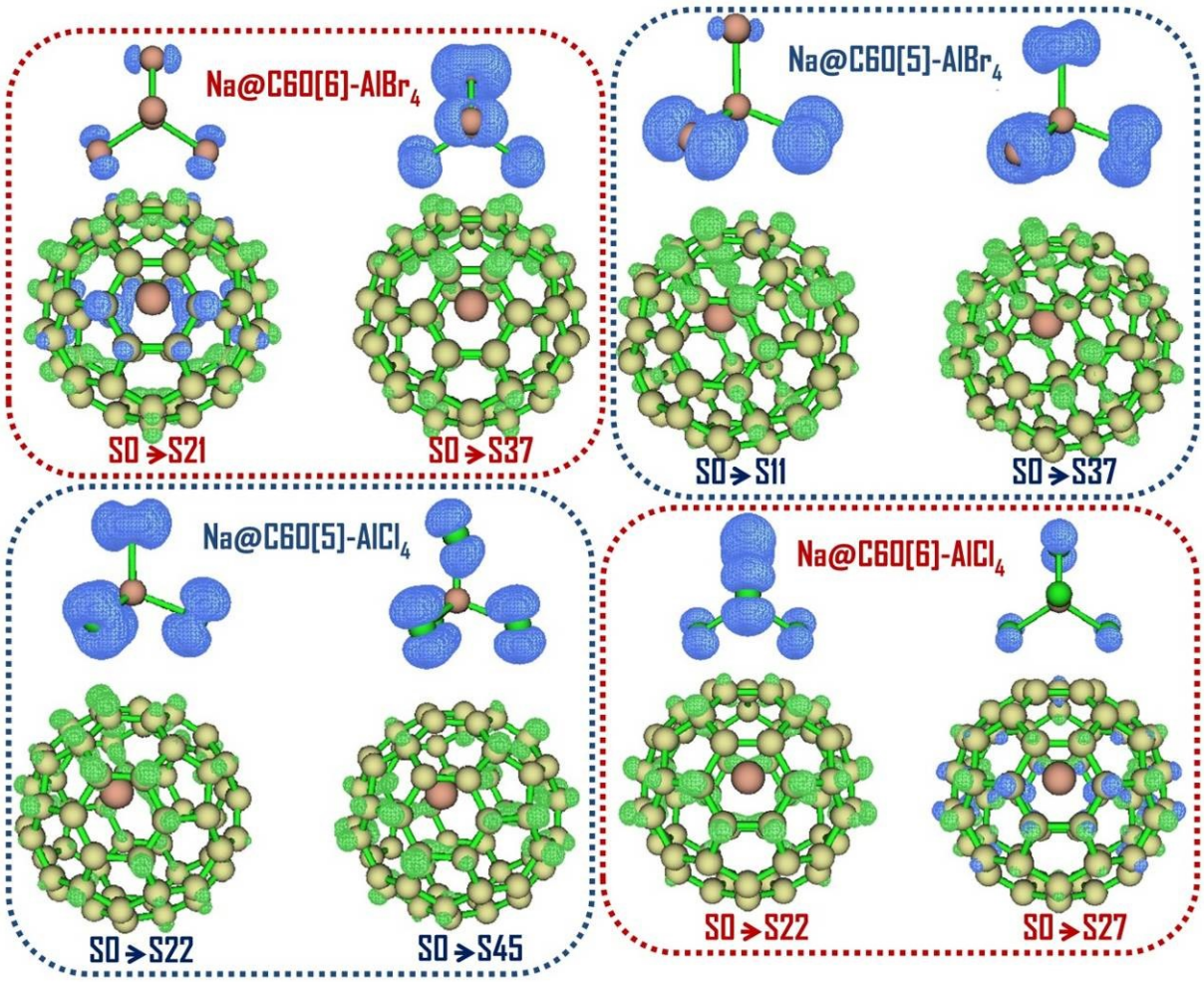

Figure. S7 Real space representations of hole and electron distribution of Na@C60[6]-AlX_4 and Na@C60[5]-AlX_4 (X=Cl,Br). Green and blue regions denote the hole and electron distributions, respectively. The isovalues of hole and electron distributions are set to be 0.002 au.

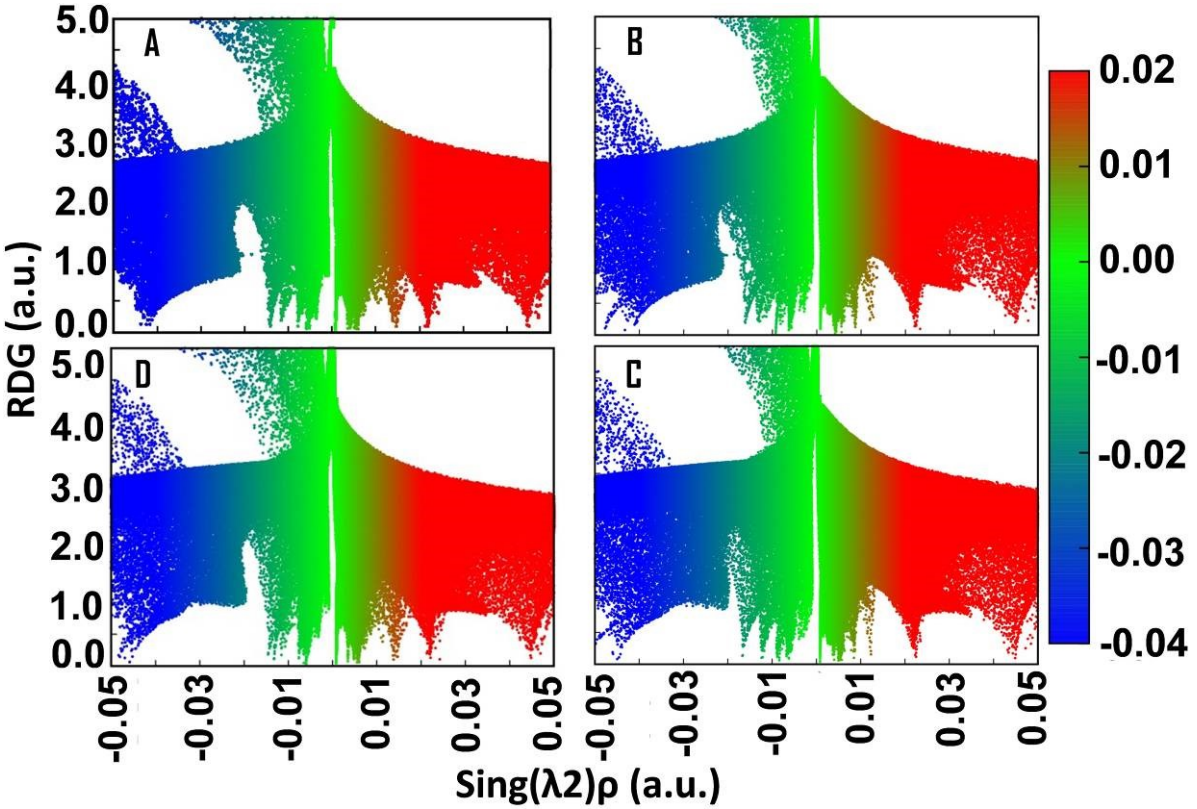

Figure. S8 Scattering graphs between the reduced density gradient and sign (λ2) of **A**) Na@C59[8-5]-$AlBr_4$, **B**) Na@C59[9-4]-$AlBr_4$, **C**) Na@C59[9-4]-$AlCl_4$ and **D**) Na@C59[8-5]-$AlCl_4$ systems.

Table S6. Polarizabilities (a.u) and (hyper)polarizabilities (a.u) in zero frequency limit and frequency-dependent fields of Na@C60[6]-AlX_4 and Na@C60[5]-Alx_4 (X=Cl,Br).

	Polarizability			***First-order hyperpolarizability***		
	α_{xx}	α_{yy}	α_{zz}	β_{xxx}	β_{yyy}	β_{zzz}
λ= ∞ nm						
C60	537.00	536.91	536.91	0.00	0.00	0.00
Na@C60[5]-$AlCl_4$	698.10	577.73	573.76	6145.07	73.50	6.53
Na@C60[5]-$AlBr_4$	789.25	603.44	603.43	-107.11	60.40	20.55
Na@C60[6]-$AlCl_4$	680.31	571.34	570.99	-2944.18	0.045	55.66
Na@C60[6]-$AlBr_4$	749.83	594.29	594.31	-5339.62	0.095	85.76
λ= 1908.54 nm						
C60	540.32	540.23	540.22	0.000	0.000	0.000
Na@C60[5]-$AlCl_4$	703.43	580.92	580.95	6503.27	75.48	6.77
Na@C60[5]-$AlBr_4$	796.89	606.77	606.77	-11551.55	61.74	20.90
Na@C60[6]-$AlCl_4$	684.65	574.35	574.01	-3067.48	0.045	57.16
Na@C60[6]-$AlBr_4$	755.37	597.39	597.45	-5673.10	0.105	89.021
λ= 1064.80 **nm**						
C60	547.98	547.89	547.89	0.000	0.000	0.000
Na@C60[5]-$AlCl_4$	716.04	588.28	528.32	7451.52	80.35	7.38
Na@C60[5]-$AlBr_4$	815.47	614.45	614.48	-13920.70	65.19	21.64
Na@C60[6]-$AlCl_4$	694.70	581.28	580.96	-3380.07	0.047	60.90
Na@C60[6]-$AlBr_4$	768.42	604.56	604.69	-6569.54	0.132	97.51
λ= 589.08 **nm**						
C60	577.20	577.10	577.09	0.00	0.00	0.00
Na@C60[5]-$AlCl_4$	769.12	616.25	616.33	13784.00	105.03	11.25
Na@C60[5]-$AlBr_4$	909.40	643.89	644.11	-37619.90	90.75	23.88
Na@C60[6]-$AlCl_4$	733.52	607.29	607.13	-5061.36	0.073	80.02
Na@C60[6]-$AlBr_4$	822.68	631.47	632.03	-12938.20	0.365	149.68

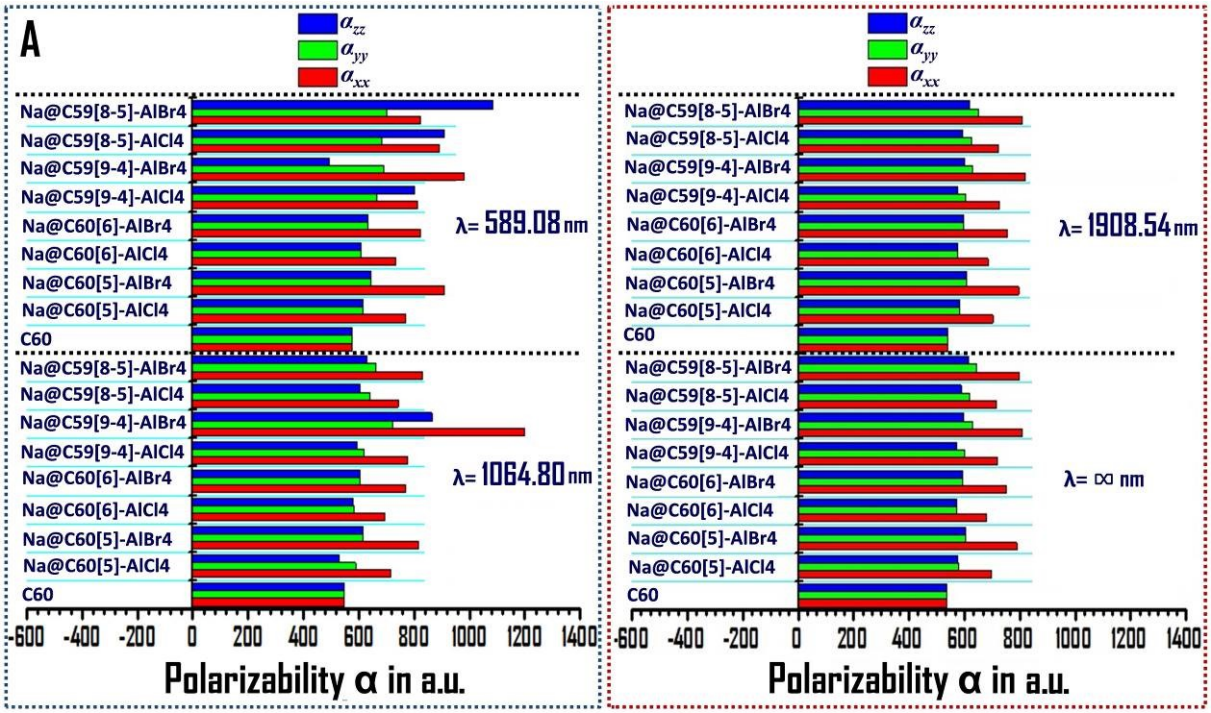

Figure. S9 Polarizabilities (α) responses of C60, Na@C60[6]-AlX_4, Na@C60[5]-AlX_4, Na@C59[9-4]-AlX_4 and Na@C59[8-5]-AlX_4 (X=Cl, Br) in zero frequency limit and frequency-dependent fields.

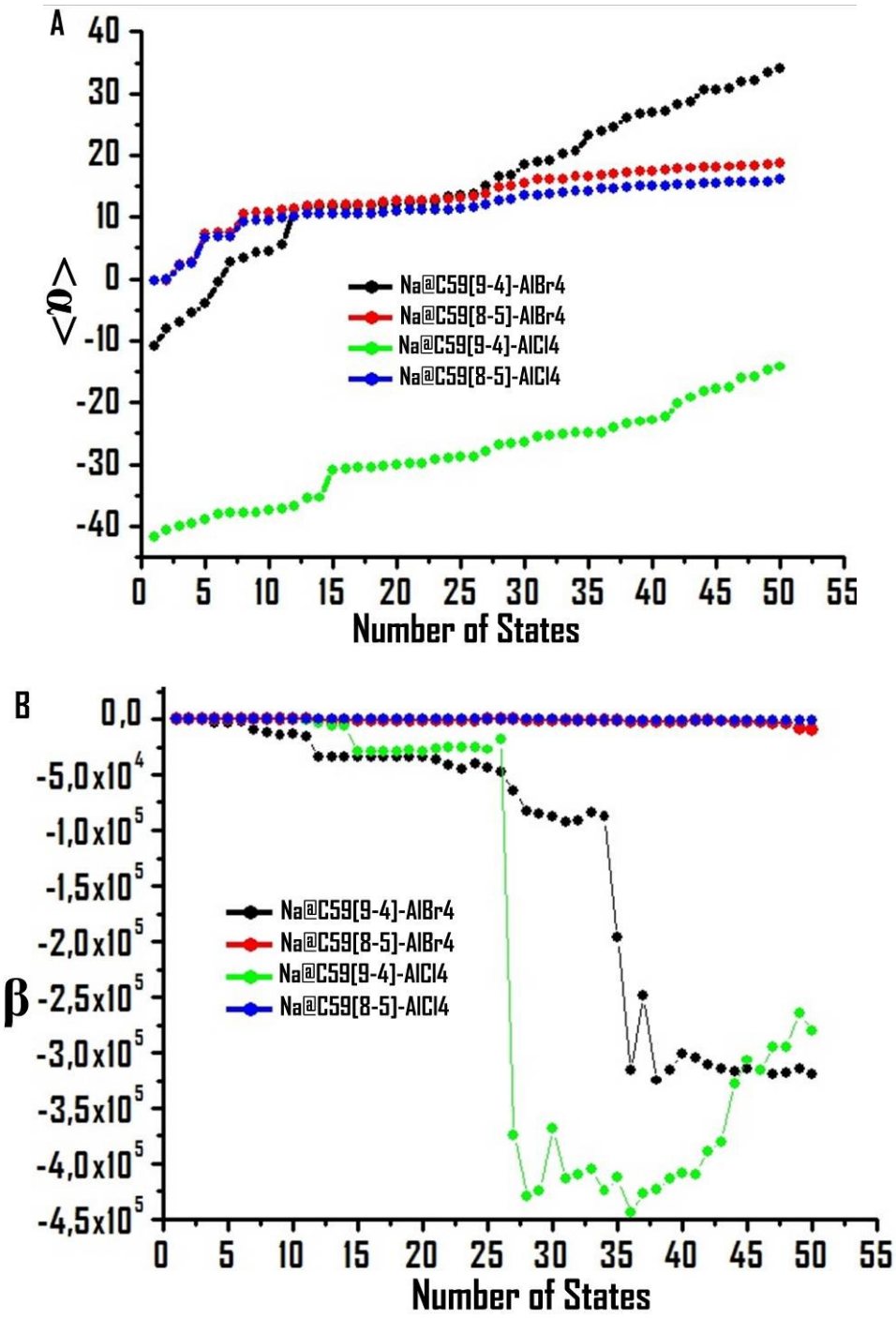

Figure. S10 Variations of **A**) Poalrizability α (λ=1064.8 nm) and **B**) Hyperpolarizability β (λ=1064.8 and 589.08 nm) with the number of states.