Design of Three-shell Icosahedral Matryoshka Clusters $A@B_{12}@A_{20}$ ($A =$ Sn, Pb; $B =$ Mg, Zn, Cd, Mn)

Xiaoming Huang1, Jijun Zhao1,2, Yan Su1, Zhongfang Chen3 & R. Bruce King4

1Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China, 2Beijing Computational Science Research Center, Beijing 100089, China, 3Department of Chemistry, Institute for Functional Nanomaterials, University of Puerto Rico, San Juan, PR 00923, USA, 4Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia, USA.

We propose a series of icosahedral matryoshka clusters of $A@B_{12}@A_{20}$ ($A =$ Sn, Pb; $B =$ Mg, Zn, Cd), which possess large HOMO-LUMO gaps (1.29 to 1.54 eV) and low formation energies (0.06 to 0.21 eV/atom). A global minimum search using a genetic algorithm and density functional theory calculations confirms that such onion-like three-shell structures are the ground states for these $A_{21}B_{12}$ binary clusters. All of these icosahedral matryoshka clusters, including two previously found ones, i.e., [As@Ni12@As20]3− and [Sn@Cu12@Sn20]5−, follow the 108-electron rule, which originates from the high $I_h$ symmetry and consequently the splitting of superatom orbitals of high angular momentum. More interestingly, two magnetic matryoshka clusters, i.e., Sn@Mn12@Sn20 and Pb@Mn12@Pb20, are designed, which combine a large magnetic moment of 28 $\mu_B$, a moderate HOMO-LUMO gap, and weak inter-cluster interaction energy, making them ideal building blocks in novel magnetic materials and devices.

The first evidence for the formation of bare anionic clusters of the post-transition elements, particularly those of groups 14 and 15, was obtained by Zintl and co-workers1–4 in the 1930s from the potentiometric titrations of post-transition elements with alkali metals in liquid ammonia. However, definitive structure determinations of these clusters became possible only in the 1970s, when Kummer and Diehl reported the first structurally-authenticated Zintl anion cluster of Na2Sn4. The original post-transition element clusters were empty, i.e., they contained no interstitial atoms in the center of the cluster polyhedron. However, subsequent synthetic studies led to the discovery of clusters containing interstitial transition metals. Examples of structurally characterized such clusters based on 10-vertex outer polyhedra include the anionic indium clusters $M@In_{10}$ (M = Ni, Pd, Pt) in the intermetallics K10In10M, the anionic lead clusters $M@Pb_{10}$ in [K(2,2,2-crypt)]$_2$[M@Pb$_{10}$] (M = Ni, Pd, Pt), $Fe@Sn_{10}$ in [K(2,2,2-crypt)$_2$[Fe@Sn$_{10}$]$_2$, the cationic pentagonal antiprismand bismuth cluster Pd@Bi$_{10}$ in Bi$_5$PdBr$_{16}$ ([Pd@Bi$_{10}$][BiBr$_{4}$])$_4$, and the centered pentagonal prismatic clusters $M@Ge_{10}$ (M = Co$^{11}$, Fe$^{11}$). Intercellular metal atoms are also found in the icosahedral M@Pb$_{12}$ clusters (M = Ni, Pd, Pt)$^{12}$. Furthermore, Al$^{11}$ has been encapsulated in Pb$_{12}^-$, Pb$_{14}^-$, and Sn$_{10}^-$ clusters, which have been characterized by mass spectroscopy and density functional theory (DFT) calculations$^{13,14}$.

Attempts to expand the knowledge of transition metal derivatives of post-transition element clusters led to the discovery of even more complicated structures. Of particular interest is the cluster $[As@Ni_{12}@As_{20}]^{3−}$, isolated as its Na$^{11}$P$^{11}$ salt and structurally characterized by X-ray diffraction$^{15}$. This cluster anion has a perfect icosahedral symmetry ($I_h$) symmetrical three-shell matryoshka doll structure consisting of an outer As$_{20}$ regular dodecahedron encapsulating an Ni$_{12}$ icosahedron, which in turn encapsulates an As$^{11}$ trianion (Figure 1). Beyond the filled d$^{10}$ shells of the arsenic and nickel atoms, this system has a total of 108 valence electrons, among which 40 skeletal electrons 16 correspond to a “magic” number of a jellium sphere$^{17}$ with 1S$^2$1P$^6$1D$^{10}$2S$^2$1F$^{14}$2P$^6$ molecular orbital configuration.

Initially the icosahedral matryoshka $[As@Ni_{12}@As_{20}]^{3−}$ structure with 108 valence electrons was considered as an anomaly, unique with an unusual combination of specific electronic and steric properties of its arsenic and nickel components. However, in 2011 Stegmaier and Fassler$^{18}$ reported a completely analogous $[Sn@Cu_{12}@Sn_{20}]^{12−}$ icosahedral matryoshka doll anion in the $M_2Cu_{12}Sn_{21}$ intermetallics (M = Na, K). This $[Sn@Cu_{12}@Sn_{20}]^{12−}$ anion is exactly isostructural with the $[As@Ni_{12}@As_{20}]^{3−}$ anion with 108 valence electrons beyond the filled d$^{10}$ shells of the tin and copper components. Similar bonding models appear to be applicable to both the $[As@Ni_{12}@As_{20}]^{3−}$ and $[Sn@Cu_{12}@Sn_{20}]^{12−}$ systems. Furthermore, the observation of the icosahedral
matryoshka doll structure in both the soluble [As@Ni_{12}@As_{20}]^{-} anion and the [Sn@Cu_{12}@Sn_{20}]^{12-} anion in the A_{12}Cu_{12}Sn_{2} inter-metallics suggests that such structures are particularly favorable in clusters where 108 total valence electrons are available from the elements composing the three layers of the matryoshka structure.

Parallel to the condensed phased clusters5 as those discussed above, gas-phase clusters have been intensively studied during the past three decades since they exhibit many fascinating physical and chemical properties that depend on their size, geometry, and composition20. Interestingly, some specific clusters with appreciable stability mimic the chemical behavior of elemental atoms in the periodic table and thus can be regarded as “superatoms”22-24. In these superatom clusters, the electronic states are delocalized over the entire cluster with spatial shapes resembling the atomic orbitals. The corresponding energy eigenvalues can be grouped into atomic-like shells (1S, 1P, 1D, 2S, 1F, 2P, …), depending on the degeneracy and spatial symmetry of the molecular orbitals. Unlike the atoms, the physical and chemical properties of superclusters can be tailored through selection of size and composition, making them very promising building blocks for new materials25,26.

The concept of “superatoms” was originally proposed by Khanna and Jena in their pioneering paper21. For example, an Al_{13} cluster with filled 1S, 1P, 1D, 2S, 1F, and 2P shells exhibits strong resistance to oxidation22. Meanwhile, with an electron affinity (EA = 3.57 eV)22 only slightly lower than that of the Cl atom (3.62 eV), a neutral Al_{13} cluster was considered as a superhalogen by Bergeron and co-workers27, though this nomenclature is not consistent with the original definition of superhalogen by Bolydyrev and Gutsev28, which defined superhalogen as a cluster/molecule whose chemical properties depend on their size, geometry, and composition22. For example, an Al_{13} cluster with an electron affinity (EA = 3.62 eV), a neutral Al_{13} cluster was considered as a superhalogen.

Table 1 | Binding energies (E_b), formation energy (E_f), HOMO-LUMO gaps (E_{HL}), optical absorption gaps (E_{og}), and the lowest allowed transition orbitals for the icosahedral matryoshka clusters A@B_{12}@A_{20} (A = Sn, Pb; B = Mg, Zn, Cd) and Pb@Mn_{12}@Pb_{20} clusters possess a giant magnetic moment of 28 \mu_B, which can be retained in cluster assemblies. Our results thus extend the scope of icosahedral matryoshka clusters and provide novel building blocks for cluster-based materials and devices exhibiting fascinating novel magnetic and optical properties.

**Results and Discussion**

The binding energies, formation energies, HOMO-LUMO gaps, and optical absorption gaps for icosahedral matryoshka A@B_{12}@A_{20} clusters (A = Sn, Pb; B = Mg, Zn, Cd) are summarized in Table 1. For a given cluster of A_{12}B_{12} its formation energy is defined as: E_f (A_{12}B_{12}) = E(A_{12}B_{12}) - xE(A) - yE(B), where E(A_{12}B_{12}) is the energy of A_{12}B_{12}, E(A) or E(B) is the energy per atom of the constituent element A or B in the standard states, x or y is the number of A or B atoms in the cluster. Detailed information on geometry parameters and on-site charges for these clusters are given in Table S1 of Supplementary Information.

All the clusters explored here show reasonably low formation energy (typically between 0.1 and 0.2 eV/atom), indicating that they are easy to form thermodynamically. For comparison, we consider several 38-atom elementary metal clusters with a fcc-like truncated octahedron structure44. Higher formation energies are obtained, i.e., 0.225 eV/atom for Pb_{38}, 0.281 eV/atom for Sn_{38}, 0.576 eV/atom for Mg_{50}, 0.497 eV/atom for Zn_{38}, and 0.385 eV/atom for Cd_{38} clusters, respectively. Using global optimization combined with DFT calculations, Ferrando’s group45 has recently achieved a series of three-shell high-symmetry matryoshka clusters, including a Ni_{13}@Mg_{20} that is isostructural to the clusters considered here. However, the formation energy of this Ni_{13}@Mg_{20} cluster is as high as 0.468 eV/atom from our DFT calculation. The more favorable formation energies of the present icosahedral matryoshka superatoms clearly demonstrate the stabilization effect of electronic structure, which will be discussed in detail later.

Note that the lengths of Pb-Pb (3.317 to 3.578 Å) and Sn-Sn (3.176 to 3.463 Å) bonds listed in Table S1 are longer than the equilibrium bond lengths of the hollow Pb_{20} (3.073 Å) and Sn_{20} (2.891 Å) cages from our DFT optimization. Therefore, the enlarged Pb_{20} and Sn_{20} cages are stabilized by the encapsulated C@B_{12} icosahedron (C = Sn, Pb; B = Mg, Zn, Cd), as previously found46 for [As@Ni_{12}@As_{20}]^{12-}. It is also interesting to compare the structural parameters of Sn@Zn_{12}@Sn_{20} with its isoelectronic counterpart, i.e., [Sn@Cu_{12}@Sn_{20}]^{12-}.

The theoretical Sn-Sn bond lengths in Sn@Zn_{12}@Sn_{20} of 3.278 Å are comparable to that of 3.290 Å for [Sn@Cu_{12}@Sn_{20}]^{12-} computed with the same level of theory. Note that the experimental Sn-Sn bond
lengths of $[\text{Sn@Cu}_{12}\text{@Sn}_{20}]^{12}\text{−}$ in the condensed phase obtained by X-ray crystallography range between 3.076 to 3.133 Å.

According to the on-site population analysis (see Supplementary Table S1), the B atoms in the intermediate shell donate some charge to the A atoms in the exterior shell, while the central A atom gains more charge, ranging from 0.245 to 1.362 electrons (by Mulliken definition). The trend of charge transfer remains the same for different systems, suggesting that all these clusters share the same pattern of chemical bonding. The direction of charge transfer can be easily understood by the electronegativity differences, that is, the Pauling electronegativities of Pb (2.33) and Sn (1.96) are higher than those of Mg (1.31), Zn (1.65), Cd (1.69), and Mn (1.55).

As shown in Table 1, the HOMO-LUMO gaps of the $A_2B_{12}$ clusters with $B = \text{Mg, Zn, Cd}$ range from 1.27 to 1.54 eV, comparable to those of $[\text{As@Ni}_{12}\text{@As}_{20}]^{3−}$ (1.44 eV) and $[\text{Sn@Cu}_{12}\text{@Sn}_{20}]^{12}\text{−}$ (1.39 eV) using the same computational scheme. Previous DFT calculations yielded similar band gaps for $[\text{As@Ni}_{12}\text{@As}_{20}]^{3−}$ (1.44 eV) and $[\text{Sn@Cu}_{12}\text{@Sn}_{20}]^{12}\text{−}$ (1.34 eV). The high symmetries of these clusters bring about multiple degeneracy of the frontier molecular orbitals and severe selection rules in optical transitions. Our TD-DFT calculations further reveal that the lowest singlet excitation (HOMO-to-LUMO) is optically forbidden due to the LUMO and HOMO symmetries. The first optically-allowed excitation (i.e., optical absorption gap $E_{\text{opt}}$) and the associated energy levels are summarized in Table 1. The computed $E_{\text{opt}}$ by TD-DFT ranges from 1.72 to 1.94 eV (i.e., the visible light region), making them potentially useful as nanoscale building blocks for optoelectronic devices.

As aforementioned, the experimentally found icosahedral matryoshka clusters, i.e., $[\text{As@Ni}_{12}\text{@As}_{20}]^{3−}$ and $[\text{Sn@Cu}_{12}\text{@Sn}_{20}]^{12}\text{−}$, are exactly isoelectronic with 108 valence electrons beyond the filled d$^{10}$ shells (for As, Ni, Sn, Cu). The same 108-electron rule applies to all binary $A_2B_{12}$ clusters considered here, noting that Mg has no d electrons. However, 108 does not explicitly belong to any existing magic numbers for various models, e.g., the shell model within the jellium approximation, the Wade-Mingos rules, the spherical aromatic model, the octet or eighteen-electron rule. Therefore, we explore the origin of the “magic number” of 108 for these spherical multi-shell clusters as a guide to design other matryoshka clusters exhibiting high stabilities and sizeable electronic gaps.

For simplicity, we start with $\text{Sn@Mg}_{12}\text{@Sn}_{20}$ that does not involve any d electrons in the valence shells of the component atoms. The energy levels and spatial distribution for the Kohn-Sham molecular orbitals of $\text{Sn@Mg}_{12}\text{@Sn}_{20}$ are presented in Figure 2 and Figure 3, respectively. According to the energetic sequence and the nodal shape of the orbitals, we can identify a series of superatom orbitals in the sequence 1S, 1P, 2S, 1D, 1F, 1G, 2P, 3S, 2D, 1H, 2F, 3P, 1I corresponding to the 54 lowest-lying valence molecular orbitals (108 valence electrons) up to and including HOMO. Among them, 1S, 1P, 2S, 1D, 1F, 2P, 3S, 2D, 3P orbitals are completely filled. In the icosahedral ligand field, the 2F, 1H and 1I superatom orbitals are split into two, three and four components, respectively. The lowest I orbital ($g_6$) is occupied as the HOMO of superatom. The lower $t_u$ component of 2F orbitals is occupied and the higher $t_u$ one is empty as LUMO + 1. Even without closure of any specific superatom orbital, a large HOMO-LUMO gap of 1.383 eV separates the occupied $g_6$ component of the 11 orbital and the empty $t_u$ component of the 1H orbital of $\text{Sn@Mg}_{12}\text{@Sn}_{20}$. Therefore, the “magic number” of 108 electrons of the icosahedral matryoshka clusters originates from the high $I_h$ symmetry and consequently the splitting of molecular orbitals of high angular momentum (2F, 1H and 1I). Previously, Martin and co-workers had shown that both electronic and geometric effects can lead to extraordinary stability for a cluster (i.e., a magic cluster).
ments in an icosahedral matryoshka cluster have to match with each other (in the range of 1.22 ~ 1.46 Å). Indeed, we have also investigated other possible icosahedral matryoshka As@B12@Sn20 clusters with B = Be, Ca (and A = Sn, Pb). However, all of them exhibited several large imaginary vibrational frequencies due to mismatch of atomic radius and thus were not further discussed here.

The energy levels for the four icosahedral matryoshka clusters, including [As@Ni12@As20], [Sn@Cu12@Sn20], [Sn@Mg12@Sn20], and Sn@Zn12@Sn20, are compared in Supplementary Figure S1. The arrangement of molecular orbitals in each species is generally similar. The differences for those clusters are related to the specific energy of each orbital as well as the relative location of the d orbitals in the Ni, Cu, or Zn derivatives. However, the d orbitals, which locate only in a narrow energy range, have no noticeable influence on the overall superatom orbitals. On the other hand, the very deep d levels for As, Sn, and Pb do not overlap with the superatom orbitals. As discussed above, the universal arrangement of molecular orbitals must originate from the unique icosahedral nested doll structure. This demonstrates further the existence of a class of matryoshka clusters with similar geometries and electronic properties.

Analogous to Cu, Ni, Zn, Cd elements with filled d⁰ shells, we further design two new icosahedral matryoshka clusters by using Mn with a half-filled d shell, that is, Sn@Mn12@Sn20 and Pb@Mn12@Pb20. According to Hund’s rule, the Mn atoms are expected to carry certain magnetic moments. Indeed, our DFT calculations show that both Sn@Mn12@Sn20 and Pb@Mn12@Pb20 possess a giant magnetic moment of 28 μB. Mulliken population analysis reveals that the magnetism mainly resides on the Mn atom, i.e., 2.880 (3.013) μB on each Mn atom for Sn12Mn12 (Pb12Mn12), whereas there are certain induced antiferromagnetic moments (about −0.3 ~ 0.8 μB) on the central and exterior Sn or Pb atoms (see Table 2). Even with the half-filled d shell and large spin polarization, these two magnetic superatoms exhibit moderate HOMO-LUMO gaps of 0.382 eV (Sn12Mn12) and 0.614 eV (Pb12Mn12), respectively, which are comparable to the gap magnitude (0.4 ~ 0.7 eV) for previously proposed magnetic superatoms, i.e., VCs8, Mn5Fe5, Ca5Fe5, MnCa5, MnSn5, TcMg8, ScK12 and ScCs12.

The spin-polarized density of states for Sn@Mn12@Sn20 and Pb@Mn12@Pb20 clusters are presented in Figure 4. Even with spin polarization, the alignments of superatom orbitals in Sn@Mn12@Sn20 and Pb@Mn12@Pb20 still resemble those of their non-magnetic counterparts shown in Supplementary Figure S1. This suggests that the 3d orbitals of Mn in such species are effectively non-bonding and contribute only to the overall magnetic moment of the clusters. As demonstrated by the spin density distribution in Figure 4(c) and (d), the magnetism mainly originates from the unpaired 3d electrons from the Mn atoms, while some superatom orbitals (like 2p, 2D, 3S) also exhibit certain exchange splitting between the majority and minority spin states. We also observe some hybridization between the 3d states of Mn and the superatom orbitals (2F, 1G, 1H, 11). Previously, Khanna and co-workers suggested that the hybridization between transition metal d states and superatom states as well as the combined action of the crystal field splitting and the exchange splitting are the key factors to stabilize a magnetic superatom and to ensure a large magnetic moment. Although the size and geometry of the current clusters are entirely different from the previous ones, this design principle for magnetic superatoms remains valid.

Previously, an [Mn@Mn12@Au20] cluster, isostructural to the current icosahedral matryoshka, was also predicted to possess a giant magnetic moment of 44 μB, but with a smaller HOMO-LUMO gap (0.25 eV). Using current theoretical scheme, the calculated formation energy for Mn@Mn12@Au20 is 0.795 eV/atom, about twice of Sn12Mn12. Again, this indicates that design of highly stable superatoms requires the consideration of electronic structures, i.e., closure of electronic shell or subshell. Also note that Sun et al. designed an onion-like caged clusters Fe8Au12@Au12 in which the magnetic moment on Fe atom (3 μB) is enhanced over bulk value, while Wu and Jena recently proposed a series of stable ferromagnetic hollow cages with large magnetic moments, i.e., Co12C6 (14 μB), Mn12C6 (38 μB), and Mn24C18 (70 μB).

In addition, a [M12] single molecular magnet, i.e., Mn12O12(CH3COO)14(H2O)4, which possesses a magnetic moment of 20 μB, has been intensively studied. To some extent, the present magnetic superatom clusters of Sn12Mn12 and Pb12Mn12 can be regarded as a kind of ligand-free single molecular magnet of [Mn12] with slightly enhanced magnetic moment (28 μB vs. 20 μB). The high symmetries, appreciable HOMO-LUMO gaps, and giant magnetic moments makes Sn12Mn12 and Pb12Mn12 clusters promising building units for novel cluster-assembled magnetic materials and devices, which have potential applications in high-density information storage, molecular spintronics, quantum computing, and magnetic resonance imaging (MRI), etc.

In the cluster-assembled materials, clusters are either encapsulated into a zeolite matrix or deposited on a substrate. It is thus crucial to examine whether every clusters in the assembly can keep their identity without coalescing into larger clusters, like the previous case of VC8. More importantly, the fantastic magnetic characteristics of the individual clusters must be well retained. As a simplest prototype of cluster assemblies, here we investigate the cluster-cluster interaction by considering the dimers of Sn@Mn12@Sn20 and Pb@Mn12@Pb20. The atomic structure and binding curve for [Pb@Pb20] dimer are shown in Figure 5 as a representative. These two clusters are stacked along a 5-fold symmetry axis with parallel pentagonal faces in a staggered orientation, which is more stable than the direct orientation by 0.180 eV. Upon formation of the dimer, there is no noticeable deformation of cluster configuration. Accordingly, the interaction strength between the two spherical dimers is rather weak, as demonstrated by the large inter-cluster distances (d = 3.787 Å for [Sn@Mn12@Sn20] and d = 4.153 Å for [Pb@Mn12@Pb20], see Figure 5) and small inter-cluster binding energies (0.359 eV for [Sn@Mn12@Sn20] and 0.291 eV for [Pb@Mn12@Pb20]). Such weak cluster-cluster interaction might be attributed to the moderate HOMO-LUMO gap as well as the sphere-like icosahedral geometry of the clusters. Most excitingly, the total magnetic moments of both cluster dimers are exactly twice of the individual ones, i.e., 56 μB. Indeed, the on-site local moments in the cluster dimers are barely affected by the neighboring cluster (see Table 2). To consider the possible antiferromagnetic state, we initially set different spin directions (spin up vs. spin down) for the Mn atoms in each of the two clusters in [Sn@Mn12@Sn20] or [Pb@Pb12@Pb20] dimer. However, upon relaxation of spin-polarized electron wavefunction, the spin state of the cluster dimer spontaneously transforms from antiferromagnetic to ferromagnetic. Moreover, inclusion of dispersion correction for the inter-cluster interaction only moderately increases the magnitude of binding energy Eint but has no effect on the magnetism of the cluster dimers. These results clearly indicate that the Sn12Mn12@Sn20 or Pb12Mn12@Pb20 clusters may keep their identities and retain their superior magnetism in cluster-assembled materials and devices. This is a vital prerequisite for their future applications.
A series of three-shell icosahedral matryoshka clusters related to the experimentally known \([\text{As}@@\text{Ni}_{12}@\text{As}_{20}]^{2-}\) and \([\text{Sn}@@\text{Cu}_{12}@\text{Sn}_{20}]^{12-}\) are proposed. A DFT-based global minimum search confirms that such icosahedral matryoshka structures are ground state configurations for these \(A_{21}B_{12}\) (\(A=\text{Sn, Pb}; B=\text{Mg, Zn, Cd}\)) binary clusters. In addition, the high stabilities of these spherical matryoshka clusters are demonstrated by their large HOMO-LUMO gaps and low formation energies. The molecular orbitals for different icosahedral matryoshka clusters share the same pattern of superatom orbitals. The “magic number” of 108 electrons can be attributed to the high \(I_h\) symmetry and consequently the splitting of superatom orbitals of high angular momentum. Such “108-electron rule” should be extendable to other icosahedral matryoshka superatoms with different charge states, which might lead to future experimental discoveries of new metal clusters in solution as well as novel solid-state intermetallic compounds. Two related magnetic icosahedral matryoshka clusters, namely \(\text{Sn}@@\text{Mn}_{12}@\text{Sn}_{20}\) and \(\text{Pb}@@\text{Mn}_{12}@\text{Pb}_{20}\), are predicted to exhibit large magnetic moments (28 \(\mu_{B}\)) and moderate HOMO-LUMO gaps. More impressively, after formation of cluster assemblies, these two clusters are able to keep their identities and retain their magnetic moments due to weak inter-cluster interaction. These novel binary clusters with unique icosahedral nesting doll geometry, high thermodynamic stabilities, and interesting physical properties (such as optical gaps in the visible region and giant magnetic moments), are expected to be useful building blocks in future nanoscale materials and devices.

**Methods**

*Ab initio* calculations were performed using the spin-polarized density functional theory as implemented in the DMol' program\(^5\). The core electrons were treated by an all-electron relativistic method including scalar relativistic effects. The generalized gradient approximation (GGA) with PW91 parameterization\(^6\) was adopted to describe the exchange-correlation interaction and the double numerical basis set including d-polarization functions (DND) were employed. Vibrational analyses were performed for each cluster to ensure that the optimized structures are the true minima on the potential energy surface. In addition, time-dependent density functional theory (TD-DFT) calculations with PW91 functional were carried out for those \(A_{21}B_{12}A_{20}\) clusters to obtain the optical adsorption spectra and optical gaps.

To confirm that the three-shell icosahedral configuration in Figure 1 is the ground state for the binary \(A_{21}B_{12}\) clusters (\(A=\text{Sn, Pb}; B=\text{Mg, Zn, Cd, Mn}\)), we performed an unbiased global minimum search of two representative clusters (\(\text{Sn}_{12}\text{Mg}_{12}\) and \(\text{Sn}_{12}\text{Zn}_{12}\)) using a genetic algorithm (GA) incorporated with DFT calculations implemented in the DMol’ package, which was described in our previous publication.
In the GA search, sixteen initial configurations were generated from scratch. Any two individuals in this population were then chosen as parents to produce a child cluster via a “cut and splice” crossover operation, followed by an optional mutation operation (either a small random displacement on each atom or exchange of a pair of different types of atoms) of 35% probability. The diversity of the populations was filtered by the inertia of each cluster. After about 3000 GA iterations, the icosahedral matryoshka structure was obtained for both Sn@Mg12@Sn20 and Sn@Zn12@Sn20 clusters as the ground state. In addition, some metastable isomers (Supplementary Figure S2) are found from GA-DFT search, but are less energetically favorable and will not be further discussed.

1. Zintl, E., Goubeau, J. & Dullenkopf, W. Metals and alloys. I. Salt-like compounds and intermetallic phases of sodium in liquid ammonia. Z. Phys. Chem., Abt. A 154, 1–46 (1931).
2. Zintl, E. & Harder, A. Metals and alloys. II. Polyplumbides, polystannides and their transition into metal phases. Z. Phys. Chem. Abt. A 154, 47–91 (1931).
3. Zintl, E. & Dullenkopf, W. Metals and alloys. III. Polyanitremides, polybismuthides and their transformation into alloys. Z. Phys. Chem., Abt. B 16, 183–194 (1932).
4. Zintl, E. & Kaiser, H. Metals and alloys. VI. Ability of elements to form negative ions. Z. Anorg. Allgem. Chem. 211, 113–131 (1933).
5. Kummer, D. & Diehl, L. Preparation and Properties of a Crystalline Compound Na2Sn10, *-6–8 Ethylenediamine. Angew. Chem., Int. Ed. 9, 895–895 (1970).
6. Henning, R. W. & Corbett, J. D. Formation of Isolated Nickel-Centered Gallium Clusters in Na10Ga10Ni and a 2-D Network of Gallium Octahedra in K2Ga3. J. Am. Chem. Soc. 133, 19758–19768 (2011).
7. Scharfe, S., Kraus, F., Stegmaier, S., Schier, A. & Fässler, T. F. Zintl Ions, Cage Compounds, and Intermetallic Clusters of Group 14 and Group 15 Elements. Angew. Chem. Int. Ed. 50, 3630–3670 (2011).
8. Jena, P. & Castleman, J. A. W. Naoclusters: a bridge across disciplines. (Elsevier, UK, 2010).
9. Khanna, S. N. & Jena, P. Assembling crystals from clusters. Phys. Rev. Lett. 69, 1664–1667 (1992).
10. Castleman, A. W. & Khanna, S. N. Clusters, Superatoms, and Building Blocks of New Materials. J. Phys. Chem. C 113, 2664–2675 (2009).
11. Jena, P. Beyond the Periodic Table of Elements: The Role of Superatoms. J. Phys. Chem. Lett. 4, 1432–1442 (2013).
12. Castleman, A. W. From Elements to Clusters: The Periodic Table Revisited. J. Phys. Chem. Lett. 2, 1062–1089 (2011).
13. Claridge, S. A. et al. Cluster-Assembled Materials. ACS Nano 3, 244–255 (2009).
14. Castleman, A. W. et al. From Designer Clusters to Synthetic Crystalline Nanoassemblies. Nano Lett. 7, 2734–2741 (2007).
15. Bergeron, D. E., Castleman, A. W., Morisato, T. & Khanna, S. N. Formation of Aln1+1 : Evidence for the superhalogen character of Al13. Science 304, 84–87 (2004).
16. Gutsev, G. L. & Boldyrev, A. I. DVM-Xs calculations on the ionization potentials of MX3+1 complex anions and the electron affinities of MX4+1 “superhalogens” Chem. Phys. 56, 277–283 (1981).
17. Bergeron, D. E., Roach, P. J., Castleman, A. W., Jones, N. O. & Khanna, S. N. Al Cluster Superatoms as Halogens in Polyhalides and as Alkaline Earths in Iodide Salts. Science 307, 231–235 (2003).
18. Kumar, V. & Kawazoe, Y. Metal-doped magic clusters of Si, Ge, and Sn: The finding of a magnetic superatom. Appl. Phys. Lett. 83, 2677–2679 (2003).
19. King, R. B. Theoretical chemistry: Magnetic superatoms. Nat. Chem. 1, 260–261 (2009).
20. Reveles, J. U. et al. Designer magnetic superatoms. Nat. Chem. 1, 310–315 (2009).
21. Zhang, X. et al. On the Existence of Designer Magnetic Superatoms. J. Am. Chem. Soc. 135, 4856–4861 (2013).
22. Medel, V. M. et al. Hund’s rule in superatoms with transition metal impurities. Proc. Nat. Acad. Sci. 108, 10062–10066 (2011).
23. Chauhan, V., Medel, V. M., Ulises Reveles, J., Khanna, S. N. & Sen, P. Shell magnetism in transition metal doped calcium superatom. Chem. Phys. Lett. 528, 39–43 (2012).
24. Medel, V. M., Reveles, J. U., Islam, M. F. & Khanna, S. N. Robust Magnetic Moments on Impurities in Metallic Clusters: Localized Magnetic States in Superatoms. J. Phys. Chem. A 117, 4297–4303 (2013).
25. Medel, V. Y., Reveles, J. U. & Khanna, S. N. Magnetism of electrons in atoms and superatoms. J. Phys. Appl. 411, 064313 (2012).
26. Pradhan, K., Reveles, J. U., Sen, P. & Khanna, S. Enhanced magnetic moments of alkali metal coated Sc clusters: New magnetic superatoms. J. Chem. Phys. 132, 124302 (2010).
27. Niemi, E. K., Niemi, G. C., Kerns, K. P. & Riley, S. J. Reactions of NiSn2 with N2H3 and CO: Cluster structure and adsorbate binding sites. J. Chem. Phys. 107, 1861–1871 (1997).
28. Damianos, K., Solokha, P. & Ferrando, R. Core-shell and matryoshka structures in MgNi nanoalloys: a computational study. J. Phys. Condens. Matter 19, 045301 (2007).
29. Zhao, J., Xie, R.-H., Tang, J., Wang, J., Lu, J.-Y., Cao, H.-Y. & Wang, J.-Y. Density functional study of onion skin-like [As4N4]2+ and [Sn4P4]4+ clusters. J. Phys. Chem. A 117, 161–166 (2004).
30. Mingos, D. M. P. Polyhedral skeletal electron pair approach. Acc. Chem. Res. 31, 311–319 (1998).
31. Hirsch, A., Chen, Z. & Jiao, H. Spherical aromaticity in H symmetrical fullerences: the 2(N+1)-1 rule. Angew. Chem. Int. Ed. 39, 3915–3917 (2000).
32. King, R. B. Chemical Applications of Topology and Group Theory, 31. Atomic Orbital Graphs and the Shapes of the g and h Orbitals. J. Phys. Chem. A 101, 4653–4656 (1997).
33. Martín, T. P., Bergmann, T., Gijbels, H. & Lange, T. Observation of electronic shells and shells of atoms in large Na clusters. Chem. Phys. Lett. 172, 209–213 (1989).
34. Cordero, B. et al. Covalent radii revisited. Dalton Trans., 2832–2838 (2008).
35. Ge, G.-X., Han, Y., Yan, J.-G., Zhao, J.-J. & Wang, G.-H. First-principles prediction of magnetic superatoms in 4d-transition-metal-doped magnesium clusters. J. Chem. Phys. 139, 174309 (2013).
48. Wang, J., Bai, J., Jellinek, J. & Zeng, X. C. Gold-Coated Transition-Metal Anion \([\text{Mn}_{13@\text{Au}_{20}}]^{2-}\) with Ultrahigh Magnetic Moment. *J. Am. Chem. Soc.* **129**, 4110–4111 (2007).

49. Sun, Q. *et al.* Effect of Au coating on the magnetic and structural properties of Fe nanoclusters for use in biomedical applications: A density-functional theory study. *Phys. Rev. B* **73**, 134409 (2006).

50. Wu, M. & Jena, P. Magnetic hollow cages with colossal moments. *J. Chem. Phys.* **139**, 044301 (2013).

51. Caneschi, A. *et al.* Alternating current susceptibility, high field magnetization, and millimeter band EPR evidence for a ground \(S = 10\) state in \([\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}\text{(H}_2\text{O})_4]\cdot2\text{CH}_3\text{COOH}\cdot4\text{H}_2\text{O}.* J. Am. Chem. Soc. **113**, 5873–5874 (1991).

52. Rogez, G. *et al.* The Quest for Nanoscale Magnets: The example of [Mn12] Single Molecule Magnets. *Adv. Mater.* **21**, 4323–4333 (2009).

53. Gubin, S. P. *Magnetic Nanoparticles.* (Wiley-VCH, Weinheim, 2009).

54. Bogani, L. & Wernsdorfer, W. Molecular spintronics using single-molecule magnets. *Nat. Mater.* **7**, 179–186 (2008).

55. Leuenberger, M. N. & Loss, D. Quantum computing in molecular magnets. *Nature* **410**, 789–793 (2001).

56. Na, H. B., Song, I. C. & Hyeon, T. Inorganic Nanoparticles for MRI Contrast Agents. *Adv. Mater.* **21**, 2133–2148 (2009).

57. Mikhailov, M. N., Kustov, L. M. & Kazansky, V. B. The State and Reactivity of Pt\(_6\) Particles in ZSM-5 Zeolite. *Catal. Lett.* **120**, 8–13 (2008).

58. Popok, V. N., Barke, I., Campbell, E. E. B. & Meiwes-Broer, K.-H. Cluster–surface interaction: From soft landing to implantation. *Surf. Sci. Rep.* **66**, 347–377 (2011).

59. Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.* **92**, 508–517 (1990).

60. Perdew, J. P. & Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**, 13244–13249 (1992).

61. Sai, L., Tang, L., Zhao, J., Wang, J. & Kumar, V. Lowest-energy structures and electronic properties of Na-Si binary clusters from \textit{ab initio} global search. *J. Chem. Phys* **135**, 184305–184309 (2011).

**Acknowledgments**
This work was supported by the National Natural Science Foundation of China (No. 11134005, 11304030), the Fundamental Research Funds for the Central Universities of China (No. DUT13ZD207, DUT14LJ19), the U. S. National Science Foundation (Grants CHE-1057466 and EPS-1010094), and the U. S. Department of Defence (Grant W911NF-12-1-0083).

**Author contributions**
J.Z. designed the models and calculations. X.H., J.Z. and Y.S. did the calculations. X.H. and J.Z. prepared all the figures. J.Z., Z.C. and R.B.K. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

**Additional information**
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Huang, X., Zhao, J., Su, Y., Chen, Z. & King, R.B. Design of Three-shell Icosahedral Matryoshka Clusters A@B\(_{12}@A_{20}\) (A = Sn, Pb; B = Mg, Zn, Cd, Mn). *Sci. Rep.* **4**, 6915; DOI:10.1038/srep06915 (2014).