RSC Advances

PAPER

Cite this: RSC Adv., 2022, 12, 13401

Received 11th March 2022
Accepted 15th April 2022
DOI: 10.1039/d2ra01591a
rsc.li/rsc-advances

Magnetic coupling induced by the interaction between endohedral metal borofullerenes†

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Superatom-assembled materials have highly tunable magnetic and electronic properties and parameters of clusters. Here, eight superatom dimers composed of two U@B40 motifs have been studied by the density functional theory. Calculation results show that U@B40 dimer exhibit spin antiferromagnetic coupling, spin ferromagnetic coupling and nonmagnetic, that is, the magnetic coupling is induced by the interaction between the U@B40 superatoms. In addition, the monomers in U@B40 dimers still retain the superatomic orbitals, and some of the super atomic orbitals disappear due to the interaction between monomers. The assembly based on U@B40 induced a decrease in the energy gap. This study provides a basis for a deep understanding of controlling the cluster-assembled materials for tailoring their functionalities.

Models and computational methods

The U@B40 has two hexagons (61 and 62) and four heptagons \( (7_1,7_4) \), as the lower right corner of Fig. 1. In this work, we enumerated various possible directions along the two U@B40 and obtained eight U@B40 dimers, and arranged them according to their total energies. Structure (a) is formed by the 7₁ heptagons of one U@B40 stacked onto the vertical 7₁ heptagons of another (denoted as 7₁∥7₁); it has the lowest total energy. Structures (b) and (c) are formed by 7₁ heptagons of one cluster parallel and antiparallel to 7₁ heptagons of another (denoted as...
73 \nabla 71 and 73 \nabla 71, respectively. Structures (d), (e), (g) and (h) are formed by the 73 heptagons or 61 hexagons of one cluster stacked onto the 61 or 62 hexagons of another. The structure (f) is formed by the B atoms of one cluster connecting to the B atoms of another cluster (represented as vertex–vertex). The relative energies between other structures and the lowest energy structure (73 \nabla 71) are placed in brackets in Fig. 1. The relative energies of the U@B40 dimers are listed in Table S1† in the ESI. Since the energy of the conformation 73 \nabla 71 is the lowest, the following analysis and discussion are mainly performed on it.

The Amsterdam density functional package (ADF, 2012.01) was employed to perform calculations. To ensure the reliability of the obtained structures, geometry optimizations were performed without imposing any symmetry constraints. All calculations presented in this work were performed using Perdew–Burke–Ernzerhof (PBE)† generalized gradient approximation exchange–correlation functionals. Scalar relativistic effects were accounted for using the zero-order regular approximation (ZORA) method. TZ2P Slater basis sets (relativistic valence triple-ζ) with two polarization functions were employed, and the frozen-core approximation was used for 1s–4f electrons of the uranium atom. The empirical dispersion-corrected density functional theory (DFT-D3)† was used to fully obtain the intermolecular interaction of the U@B40 structures.

Results and discussion

The spin polarization of U@B40 dimers was analyzed and the results were different from those of U@B40 without spin polarization. As shown in Fig. 2, the spin orientation of one U@B40 monomer in the 73 \nabla 71, 73 \nabla 71 and 61–62 conformations is spin-up, and that of another monomer is spin-down. The spin orientations of the two monomers are opposite, thus exhibiting the spin antiferromagnetic coupling phenomenon, which is consistent with (U@C28)2. For 73 \nabla 71, vertex–vertex and 73–62, conformations, the spin orientations of the two U@B40 monomers are spin-up, and thus exhibiting spin ferromagnetic coupling. Distinct from 73–62, although the ground state of 73–61 conformation is also a triplet state, the two unpaired electrons are occupied on one monomer. Thus, one U@B40 monomer exhibits spin polarization, while another monomer has no spin polarization (shown in Fig. 2(d)). In addition, the ground state of the 61–61 structure is a closed-shell singlet state without spin polarization, similar to U@B40. The results show that different U@B40 dimers exhibit different spin polarization phenomena, thus U@B40 as the motif for assembly can affect the magnetic properties.

To further explore the origin of the spin-polarized phenomenon, the MOs of U@B40 dimers were analyzed. There are 232 α and 232 β MOs of the conformation 73 \nabla 71, and the frontier MOs diagram is shown in Fig. 3. The HOMO for the α electron (denoted as HOMOα) is strongly localized on one U@B40 conformation and that of another monomer is spin-down. The spin orientations of the two monomers are opposite, thus exhibiting the spin antiferromagnetic coupling phenomenon, which is consistent with (U@C28)2. For 73 \nabla 71, vertex–vertex and 73–62, conformations, the spin orientations of the two U@B40 monomers are spin-up, and thus exhibiting spin ferromagnetic coupling. Distinct from 73–62, although the ground state of 73–61 conformation is also a triplet state, the two unpaired electrons are occupied on one monomer. Thus, one U@B40 monomer exhibits spin polarization, while another monomer has no spin polarization (shown in Fig. 2(d)). In addition, the ground state of the 61–61 structure is a closed-shell singlet state without spin polarization, similar to U@B40. The results show that different U@B40 dimers exhibit different spin polarization phenomena, thus U@B40 as the motif for assembly can affect the magnetic properties.

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monomer, while the HOMO for β electron (HOMOβ) mainly occupies another monomer. The other occupied MOs were delocalized on the U@B_{40} dimer. Therefore, the spin density of 7_{3,1,7_{1}} conformations is mainly contributed by HOMOα and HOMOβ. The spin density for spin-up comes from HOMOα, while that for spin-down derives from HOMOβ, thus exhibiting spin antiferromagnetic coupling. Furthermore, the MOs of other U@B_{40} dimers were also analyzed, and the results show that the spin density comes from the frontier MOs of structures [as shown in Fig. S1–S7†].

Previous studies on B_{40} oligomers have shown that B_{40} monomers still retain superatomic properties.24 Similarly, the superatomic MOs of 7_{3,1,7_{1}} conformations were also analyzed in detail. In the MOs with lower energy levels, we found that the monomeric superatomic orbitals are composed of B_{40} cages. While superatomic orbitals are contributed by the 2s orbital of B atoms, similar to the superatomic orbital 1S, 1P, 1D and 1F of B_{40} (ref. 33) (as shown in Fig. 4). The superatomic MOs of two monomers cooperate in in-phase and out-of-phase cooperation, denoted as 1S–1S, 1P–1P, 1D–1D, 1F–1F. In the MOs with higher energy levels, the U@B_{40} monomer still retains superatomic MOs, and the superatomic orbitals are a hybridization of the 7s, 7p, 6d, and 5f orbitals of the U atom with the B_{40} cage orbitals.35 The superatomic MOs of two U@B_{40} monomers cooperate in in-phase and out-of-phase, denoted as 2S–2S, 2P–2P, 2D–2D, 2F–2F, as shown in Fig. 5. However, U@B_{40} exhibits a 32-electron closed-shell singlet configuration.35 There should be two 5–s, six P–P, ten D–D and fourteen F–F superatomic MOs in accordance with the in-phase and out-of-phase cooperation between each other. Here, we found that some monomeric superatomic orbitals disappeared due to the stronger orbital interaction. The disappearance of 1D–1D MOs is caused by the distortion of the B_{40} cages and the disappearance of 2D–2D and 2F–2F MOs result from the deviation of the U atom from the cage center. Fig. 4 and 5 are the superatomic MOs diagrams of α electrons, and the superatomic MOs diagrams of β electrons are shown in Fig. S8 and S9† in ESI. In addition, we also analyzed the MOs of

Fig. 4 The MOs diagram for α electrons of 7_{3,1,7_{1}} confirmations for the U@B_{40} superatomic orbital components. Superatomic orbitals 1S, 1P, 1D, and 1F are composed of the B_{40} cages. The blue and red areas indicate the positive and negative signs of the wave functions, respectively. Isovalue = 0.02 a.u.

Fig. 5 MOs-α of the 7_{3,1,7_{1}} conformations for the U@B_{40} superatomic orbital components. 2S, 2P, 2D, and 2F refer to the U@B_{40} monomer superatomic orbitals.

Fig. 6 Density of states of structure 7_{3,1,7_{1}}. (a) The total density of states (TDOS) of 7_{3,1,7_{1}} and the local density of states (LDOS) of U atoms. (b) and (c) The partial density of states (PDOS) of s, p, d, and f atomic orbital of two U atoms.
Conclusions

In this study, U@B_{40} superatom dimers were investigated using the first principles. The results show that different U@B_{40} dimers exhibit different spin polarization phenomena, they have spin antiferromagnetic coupling, spin ferromagnetic coupling and nonmagnetic. As such, the magnetic coupling can be tuned according to different types of the U@B_{40} assembly. Moreover, the spin density mainly comes from the frontier MOs. Further analysis of the MOs revealed that the monomer of the U@B_{40} dimers still retained some superatomic properties. One kind of superatomic orbital is composed of B_{40} cages and another kind of superatomic orbital is composed of B_{40} and U atoms. In addition, the U@B_{40} superatomic assembly causes the energy gap to decrease. This work mainly studied the interaction between embedded metal fullerences, which provides a new idea for cluster assembly materials.

Author contributions

Jia Wang calculated and analyzed the results. All the authors contributed to the general discussion.
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