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**ThC$_2$@C$_{82}$ versus Th@C$_{84}$: unexpected formation of triangular thorium carbide cluster inside fullerenes**

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Synthesis of the first thorium-containing clusterfullerenes, ThC$_2$@C$_6$–C$_{82}$ and ThC$_2$@C$_5$–C$_{82}$, is reported. These two novel actinide fullerene compounds were characterized by mass spectrometry, single-crystal X-ray diffraction crystallography, UV–vis–NIR spectroscopy, and theoretical calculations. Crystallographic studies reveal that the encapsulated ThC$_2$ clusters in both C$_6$–C$_{82}$ and C$_5$–C$_{82}$ feature a novel bonding structure with one thorium metal center connected by a C$_{2s}$C$_s$ unit, forming an isosceles triangular configuration, which has not been hitherto observed for endohedral fullerenes or for solid phase thorium carbides. Electronic structure calculations assign a formal electronic structure of [Th$_4$+(C$_2$)$^3_2^1$]$^2_1@$[C$_{82}$]$^1$, with pronounced donation bonding from (C$_2$)$^3_2^1$ to Th$_4$$^+$, secondary backbonding from the fullerene to thorium and Th–C double bond character in both compounds. This work presents a new family of endohedral fullerene, MC$_2$@C$_{2n+2}$, being unexpected isomers of MC$_2$$_{2n}$, and provides broader understanding of thorium bonding.

**Introduction**

Fullerenes are known for their ability to encapsulate clusters, which results in the formation of unique host–guest molecular compounds—endohedral clusterfullerenes.$^{1-3}$ The unique interaction and mutual stabilization between the metal-containing clusters and fullerenes gave rise to fascinating electronic structures and potential applications of these compounds.$^{4-7}$ To date, most lanthanides have been encapsulated in fullerene cages.$^8$ Our recent research showed that novel actinide clusters can also be captured and stabilized by fullerene cages, such as U$_2$C@I$_n$(7)–C$_{80}$, U$_2$C$_2$@I$_n$(7)–C$_{80}$, or UCN@C$_{82}$.$^{9-11}$ These systems exhibit substantially different electronic structures compared to known lanthanide-based analogs. In particular, the encapsulated uranium clusters reveal bonding properties that have never been observed in conventional uranium compounds. Thus, the exploration of novel actinide cluster fullerenes will not only expand the scope of endohedral fullerenes, but also have significance regarding the understanding of fundamental actinide chemistry. However, all of the actinide cluster fullerenes discovered thus far were based on uranium; other actinide cluster fullerenes have yet to be explored.$^{12}$

Thorium is arguably the new frontier of nuclear energy.$^{13}$ Attempts have been made to synthesize and characterize thorium compounds for use as potential fuels in advanced reactors. Recently, thorium carbides have attracted increasing attention because these compounds are suitable for high-burnup and high-temperature operations with increased “margin to melting” in the framework of modern nuclear systems.$^{14}$ Many advantages of thorium carbides, such as high melting points, corrosion resistivity, low thermal expansion coefficients and high thermal conductivity, have been reported in recent research.$^{15,16}$ Therefore, understanding the behavior and properties of thorium carbides is essential to explore their potential application as nuclear reactor fuel materials.$^{17,18}$

Thorium carbides (ThC$_{2n}$, $n = 1–6$) have been detected in vapors above solid carbides or metal alloys in graphite systems, and partial pressures of thorium carbides were measured by mass spectrometry.$^{19–22}$ Thorium dicarbide (ThC$_2$), as the main type of stoichiometric thorium carbides, exists in polymorphic modifications at ambient pressure.$^{16,21}$ However, the structural and electronic properties of ThC$_2$ have only been studied by theoretical calculations.$^{18,21,26}$ Thus far, the molecular structure of ThC$_2$ has not been observed in the condensed phase.

On the other hand, carbide cluster fullerenes (CCFs) are an important branch of endohedral cluster fullerenes and have
been extensively investigated in the past two decades. The first reported CCF is ScC2@D2d(23)−C84, initially assigned as a di-metallofullerene (EMF), ScC2@C86. This discovery confirmed that the composition M2C2n could exist as M2C2n or as M2C2@C2n−2. Subsequent studies revealed a large family of CCFs with variable M2C2 clusters encapsulated inside different fullerene cages, such as Sc2C2@C2n2−27, Gd2C2@C2n2−2, Lu2C2@C2n2−2 et al.2 In addition, composition Sc2C82 was also reassigned as Sc2C2@Ik−C86.33 Up to now, a large variety of CCFs entrapping multiple (2–4) metal atoms have been reported. However, monometallic carbide cluster fullerenes have not been yet available and whether M@C84 can exit as MC2n or as MC2@C2n−3 has yet to be explored.

Herein, we report the first thorium-based cluster fullerenes, namely, ThC2@C6(6)−C82 and ThC2@C5(5)−C82. Crystallographic studies reveal that, these two actinide endohedral fullerences, initially assigned as isomers of Th@C84, are in fact thorium-based cluster fullerenes which contains a unique mononuclear thorium carbide cluster. Theoretical analyses confirm that ThC2@C6(6)−C82 and ThC2@C5(5)−C82 can be described by a formal two-electron transfer from the ThC2 cluster to the C82 cage, which results in formal closed-shell electronic structures $\text{[Th}^4+\text{(C}_2)^2\text{]}^2^−@\text{[C}_8\text{]}^2^−$.

**Results and discussion**

**Synthesis and isolation of ThC2@C6(6)−C82 and ThC2@C5(5)−C82**

Thorium-based endohedral metallofullerenes were synthesized by a modified Krätschmer−Huffman DC are discharge method. Graphite rods packed with UO2/ThO2 and graphite powder (molar ratio of U: Th: C = 1:1:30) were vaporized in the arcing chamber under a 200 Torr He atmosphere. The resulting soot was then collected and extracted with CS2 for 12 h. A series of thorium-containing endohedral metallofullerenes were generated from this process (Fig. S2†) and in this work, two novel isomers(1n) of ThC84 (later assigned as ThC2@C6(6)−C82 and ThC2@C5(5)−C82) were isolated by a multistage high-performance liquid chromatography (HPLC) separation process (Fig. S1†). The purity of the isolated compounds was confirmed by positive-ion-mode matrix-assisted laser/desorption ionization time-of-flight mass spectrometry (MALDI-TOF/MS), as shown in Fig. 1. The mass spectra of ThC2@C6(6)−C82 and ThC2@C5(5)−C82 show peaks at m/z = 1240.196 and 1240.204. In addition, the experimental isotopic distributions of the two samples agree well with theoretical predictions.

**Molecular and electronic structures of ThC2@C6(6)−C82 [NiIOEP] and ThC2@C5(5)−C82 [NiIOEP]**

Two black block cocrystals were obtained by slow diffusion of [NiIOEP] (OEP = 2,3,7,8,12,13,17,18-octaethylporphin dianion) in benzene into a CS2 solution of the corresponding compounds. NiIOEP was used to hinder rotation of fullerene molecules in the co-crystal. The molecular structures of ThC2@C6(6)−C82 [NiIOEP] and ThC2@C5(5)−C82 [NiIOEP] were determined by single-crystal X-ray diffraction analysis, excluding other molecular structures with the same molecular weight, such as Th-based mono-metallofullerenes, Th@C84 isomers. The shortest Ni-cage distance was measured as 2.846(104) and 2.855(115) A for ThC2@C6(6)−C82 [NiIOEP] and ThC2@C5(5)−C82 [NiIOEP], indicating a strong π–π interaction between ThC2@C5(5)−C82 and NiIOEP. Both ThC2@C6(6)−C82 [NiIOEP] and ThC2@C5(5)−C82 [NiIOEP] were solved in the monoclinic space group C2/m.

The whole molecule of ThC2@C6(6)−C82 including the fullerene cage and the encapsulated cluster, shows two equivalent orientations with the same occupancy of 0.5, which is common in many analogous metallofullerenes/NiIOEP co-crystal systems.1 The encapsulated Th ion shows only slight disorder with a total occupancy of 0.5 for the three disordered sites Th1−Th3. Th1 is assigned as the major Th site, as it has a much higher occupancy of 0.418 compared to those of the other two sites (0.0489 and 0.0326 for Th2 and Th3, respectively). Furthermore, Th1A, Th2A and Th3A are also generated via their mirror-related counterparts, Th1, Th2 and Th3, due to the same crystallographic mirror plane. Further structural analysis shows that Th1 is situated on the symmetry plane of the C6(6)−C82 cage, while Th1A is located away from the symmetry plane (Fig. S4†). The density functional theory (DFT) calculation results also suggest that the Th1 site is approximately 13 kcal mol−1 lower in energy for all functionals than Th1A (Table S2†). In addition, previous studies suggest that the metal ion prefers to remain symmetrically aligned with interacting motifs that share one of the symmetry planes with the fullerene containing mirror planes.4 Therefore, we assign Th1 as the optimal position of ThC2@C6(6)−C82 (Fig. 2a).

The crystallographic results of ThC2@C5(5)−C82 also show two orientations of the fullerene molecule with equal occupancy of 0.5. These two orientations are related by the molecular crystallographic mirror. The Th1 site is the major Th position for ThC2@C5(5)−C82, with a fractional occupancy of 0.281. Th1A has the same occupancy of 0.281 and is symmetrical with Th1 through a crystallographic mirror. The rest of the minor sites are displayed in Fig. S3(b).† Th1 is located beneath the corresponding hexagon, with the shortest metal-cage distances of 2.542(12) Å (Th1–C3) and 2.589(13) Å (Th1–C2). Its mirror-related counterpart, Th1A, on the other hand, has the closest...
The ThC2 cluster in C2(6)–C82 features two almost identical Th–C distances, 2.360(11) and 2.353(10) Å, respectively, leading to an isosceles triangular configuration. ThC2 in C2(5)–C82 has a similar but slightly distorted isosceles triangular configuration, with a Th–C bond length difference of 0.05 Å. Note that the metal–C\textsubscript{cage} distances in the two ThC2@C82 isomers, as mentioned already, are also somewhat different [2.546(13)–

As shown in Fig. 2c and d, the Th–C distances are 2.360(11)/2.353(10) Å for ThC2@C2(6)–C82 and 2.334(15)/2.385(14) Å for ThC2@C2(5)–C82, which are significantly shorter than the Th–C single bonds in thorium-based organometallic complexes (2.471–2.892 Å),\textsuperscript{35,36} as shown in Table 1. Moreover, for the encapsulated cluster ThC2, the C–C distances from the X-ray diffraction are 1.168(16) Å and 1.11(2) Å in the C2(6)–C82 and C2(5)–C82 cages, respectively, as shown in Table S3.\textsuperscript{†} These C–C bonds can be assigned as triple bonds, but they are approximately 0.1 Å shorter than the optimized distances obtained by theoretical calculations (1.252 and 1.251 Å), respectively, of the isolated cluster fullerenes. The unusual phenomenon of shrinking C–C bonds inside fullerene cages has also been observed for metal carbide cluster fullerenes such as ScC2@D10(14 246)–C74, Ga2C2@D10(85)–C82 and U2C2@D10(5)–C76, in which the X-ray crystallographically determined C–C bond lengths (1.049(17) Å,\textsuperscript{19} 1.04(2) Å (ref. 38) and 1.127(18) Å (ref. 10) respectively) are also notably shorter than the C–C triple bonds in alkyne compounds (1.21 Å). In addition, as shown in Fig. 2c and d, the metal–C\textsubscript{cage} distances are 2.546(13)–2.736(17) Å for ThC2@C2(6)–C82 and 2.543(13)–2.687(17) Å for ThC2@C2(5)–C82, which agree well with the theoretical calculations (Table S3)\textsuperscript{†} (2.506–2.814 Å for ThC2@C2(6)–C82 and 2.635–2.686 Å for ThC2@C2(5)–C82). These distances are similar to the Th–Cp(cent) distances in organometallic compounds; for example, the Th–Cp(cent) distances are 2.532(4)–2.649(8) Å in actinide phosphinidene metalloccene (Cp = cyclopentadienyl ring).\textsuperscript{39,40} This result suggests that the coordination interaction between Th and the fullerene cage may be similar to that between Th and the cyclopentadienyl group in organometallic compounds.

The ThC2 cluster in C2(6)–C82 features two almost identical Th–C distances, 2.360(11) and 2.353(10) Å, respectively, leading to an isosceles triangular configuration. ThC2 in C2(5)–C82 has a similar but slightly distorted isosceles triangular configuration, with a Th–C bond length difference of 0.05 Å. Note that the metal–C\textsubscript{cage} distances in the two ThC2@C82 isomers, as mentioned already, are also somewhat different [2.546(13)–

| System | Th···C distance (Å) | Ref. |
|--------|---------------------|-----|
| ThC2@C2(6)–C82 | 2.360(11)/2.353(10) | This work |
| ThC2@C2(5)–C82 | 2.334(15)/2.385(14) | This work |
| [1,3-((SiMe3)C3H3)2]Th | 2.643(10)/2.687(11) | 35 |
| [1-(SiMe3)C3H4]4Th | 2.576(14) | 36 |
| [C2Me5]3ThMe2 | 2.471(8)/2.478(9) | 36 |
| [C3Me5]3Th(CH2Ph)2 | 2.552(7)/2.551(7) | 36 |

Fig. 2  ORTEP drawing of ThC2@C2(6)–C82: [NiIIOEP] (a) and ThC2@C2(5)–C82: [NiIIOEP] (b) with 20% thermal ellipsoids. Only the predominant Th (Th1) sites are shown. For clarity, the solvent molecules and minor metal sites (Fig. S3) are omitted. Fragment view showing the interaction of the ThC2 clusters with the closest aromatic ring fragments of the C2(6)–C82 cage (c) and C2(5)–C82 cage (d).
C84, as shown in Fig. 4 suggests that the encapsulated mono-
the symmetric triangular isolated ThC2 molecule obtained in
of the ThC2 cluster encapsulated in either C2(5) or C2(6)
isomers. The Sym ThC2@C2(5)
fullerene cage, as discussed later.

A closer look at the symmetric structure of ThC2@C2(6)–C82 shows that, although the encapsulated ThC2 can have many possible orientations relative to the cage, both the metal atom, Th1, and the cluster, Th2, are located right on the symmetry plane. Further analysis of the crystallographic data of other mononuclear cluster fullerene-containing symmetry planes, such as MCN@C2(6)–C82 (M = U, Y and Dy), MCN@C2(9) – C82, DyCN@C2(9)–C82 and DyCN@C2(17)– C82, as shown in Fig. 4 suggests that the encapsulated mononuclear clusters are all located on the mirror planes of fullerene cages (see Fig. 3). Previous studies of monometallic fullerenes (only one metal ion inside the cage) have found that in fullerene cages containing symmetry planes, the metal prefers to occupy a symmetric arrangement with respect to the interacting motifs, which share one of their symmetry planes with the fullerene. This observation further suggests that the endohedral mononuclear cluster also prefers to share a symmetry plane with the fullerene cages. That is, in general, as long as the fullerene encapsulating a mononuclear cluster possesses mirror planes, the entire molecule tends to be symmetric.

The identification of the encapsulated ThC2 cluster expands our understanding of endohedral fullerenes. It represents a new type of endohedral cluster MCn, in which a single metal ion is coordinated to a C≡C unit. In previous fullerene studies, if a fullerene compound was identified by mass spectrometry as MC2n, it can be intuitively assigned as a mono-metallofullerene, i.e., M@C2n, in which only a single metal ion is encapsulated inside the cage. The discovery of MC2n, however, breaks this paradigm and suggests that MC2n can also be the isostuctural isomer of MC2@C2n–2. Moreover, it provides the first crystallographic observation of a discrete ThC2, which may be beneficial for the better understanding of those thorium carbide gas molecules generated in high temperature.

Theoretical investigation

DFT calculations for ThC2@C2(6)–C82 and ThC2@C2(5)–C82 identified spin-singlet ground states. It is known that C82 can accept two electrons, for example, in the case of Sm@C82 and TbCN@C82 [C82(6) and C82(5) isomers]. Based on the frontier molecular orbitals in our calculations, we verified that there is a transfer of two electrons from the encapsulated ThC2 cluster to the C82 cage, i.e., the system adopts a formal closed-shell [ThIV(C2)2]2−@[C82]2− electron configuration. Therefore, we interpret that ThC2@C82 isomers have similar two-electron transfer to those of Sm@C82 and TbCN@C82. In all three cases, isomeric structures of C82(6)–C82 and C82(5)–C82 are stabi-
ized by the metal/cluster-to-cage two electron transfer. For the spin-singlet states, the structural parameters optimized with the B3LYP hybrid functional match the experimental data.
better than other tested functionals. The following discussion is based on all-electron scalar relativistic B3LYP optimizations and the corresponding electronic structures.

The metal–ligand bonding in ThC2@C6(6)−C82 and ThC2@C2(5)−C82, was characterized in terms of natural localized molecular orbitals (NLMOs) and Wiberg Bond Orders (WBOs). In ThC2@C6(6)−C82, as shown in Fig. 3, there are three pairs of NLMOs, one σ and two π, describing the formal triple bond of C2. There is pronounced covalency with thorium. The two π NLMOs display three-center characteristics involving Th, with 10% and 9% weights of the orbital density associated with Th 6d and C2. The WBO of 0.85 is close to the bond donating, with 13% weight at thorium. The WBO for C2−C82 shows broad peaks at 673, 752, 905, 1040, and 1292 nm and a shoulder peak at 484 nm, similar to those of TbCN@C6(6)−C82.46 For ThC2@C2(5)−C82, the characteristic absorption peaks were observed at 621, 650, 767, 907, and 1036 cm−1, almost identical to those of TbCN@C2(5)−C82 with the same fullerene cage.46 This indicates similar cage isomer and electronic transfer between ThC2@C2(5)−C82 (right) and TbCN@C2(5)−C82, which is consistent with the results obtained from single-crystal X-ray diffraction and the computational results for [ThC2] +@C82.

Conclusions

For the first time, thorium clusters were encapsulated inside fullerene cages. ThC2@C6(6)−C82 and ThC2@C2(5)−C82 were synthesized and characterized by mass spectrometry, single-crystal X-ray diffraction crystallography, UV–vis–NIR spectroscopy, and DFT calculations. Crystallographic studies reveal that a mononuclear carbide, which has never been found in endohedral fullerenes, is stabilized inside a C82 cage. The two Th–C bond lengths of the ThC2 cluster encapsulated in both C6(6)−C82 and C2(5)−C82 are 2.30(11)/2.353(10) Å and 2.334(15)/2.385(14) Å, presenting isoceles triangular configurations, although the latter shows slight distortion, likely affected by the different cage isomeric structures.

DFT calculations for two isomers of ThC2@C82 revealed that the electronic structure can be described as a spin singlet ground state, formally [Th4+(C2)2] +@C82, with pronounced donation bonding from C2 to Th4+ and secondary back-bonding from the fullerene to thorium. The triangular cluster [ThC2]2+ is more stable in the C6(6)−C83 cage (1a) than in the C2(5)−C82 cage (2a), which is in part rationalized by a weaker backbonding in the latter. Theoretical analysis also shows a triple bond in the C2− fragment that is somewhat weakened by the donation to the metal. The calculations provide an intuitive description of the bonding of actinide and main group atoms as they are encapsulated in fullerenes.

This work expands the scope of both endohedral fullerenes and actinide compounds. ThC2@C82 represents a new family of endohedral fullerenes, which reveals for the first time that MC2n fullerences, the most commonly observed endohedral fullerenes, may have two isomeric structures, namely, M@C2n versus MC2n@C2n. Furthermore, identification of the unique bonding motif of ThC2 deepens our understanding of the chemical bonding of thorium.

Experimental section

Spectroscopic study

Positive-ion mode matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker, Germany) was employed for mass characterization. The UV–vis–NIR spectra of the purified ThC2@C82 were measured in C82 solution with a Cary 5000 UV–vis–NIR spectrophotometer (Agilent, USA).
X-ray crystallographic study

The black block crystals of ThC₂@C₆(6)·C₆₂ and ThC₂@C₅(5)·C₆₂ were obtained by slow diffusion of the CS₂ solution of the corresponding metallofullerene compounds into the benzene solution of [Ni⁺(OEP)]. Single-crystal X-ray data of ThC₂@C₆(6)·C₆₂ and ThC₂@C₅(5)·C₆₂ were collected at 120 K on a diffractometer (Bruker D8 Venture) equipped with a CCD collector. The multiscan method was used for absorption correction. The structures were solved using direct methods and refined on F² using full-matrix least-squares using the SHELXL2015 crystallographic software packages. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Crystal data for ThC₂@C₆(6)·C₆₂·[Ni⁺(OEP)]·2C₆H₆ and ThC₂@C₅(5)·C₆ɂ·[Ni⁺(OEP)]·2C₆H₆ are provided in Table S4.†

Computational details

Kohn–Sham density functional calculations were performed for ThC₂@C₆(6)·C₆₂ and ThC₂@C₅(5)·C₆₂ structures with the 2017 release of the Amsterdam Density Functional (ADF) suite. Different functionals, including the Perdew–Burke–Ernzerhof (PBE) and Becke–Perdew (BP86) nonhybrid functional, a global hybrid based on PBE with 25% exact exchange (PBE0), and the popular B3LYP hybrid functionals, were used in conjunction with all-electron Slater-type atomic orbital (STO) basis sets of triple-ζ polarized (TZP) quality for the geometry optimizations and electronic structure analyses. Relativistic effects were considered by means of the scalar-relativistic Zeroth-Order Regular Approximation (ZORA) Hamiltonian. An atom-pairwise correction for dispersion forces was considered via Grimme’s D3 model augmented with Becke–Johnson (BJ) damping. To quantify the compositions of the chemical bonds for selected optimized systems, natural localized molecular orbital (NLMO) analyses were carried out with the NBO program, version 6.0, interfaced with ADF.

Data availability

CCDC 2183932 and 2183933 contain the supplementary crystallographic data for this paper.† These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/data_request/cif. All other data supporting the findings of this study are available from the corresponding authors on request.

Author contributions

N. C. conceived and designed the experiments. Y. S. and Q. M. synthesized and isolated all the compounds. J. A. and X. Y. performed the computations and theoretical analyses. Y. S. and Q. M. performed the single-crystal measurements. Y. Y. and Y. S. performed the crystallographic analysis. Y. S. performed the spectroscopic measurements. N. C., J. A., Y. S., X. Y., Q. M. and Y. Y. co-wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 A. A. Popov, S. Yang and L. Dunsch, Chem. Rev., 2013, 113, 5989–6113.
2. S. Yang, T. Wei and F. Jin, Chem. Soc. Rev., 2017, 46, 5005–5058.
3. W. Shen, S. Hu and X. Lu, Chem.–Eur. J., 2020, 26, 5748–5757.
4. G. Velkos, W. Yang, Y. R. Yao, S. M. Sudarkova, X. Liu, B. Buchner, S. M. Avdoshenko, N. Chen and A. A. Popov, Chem. Sci., 2020, 11, 4766–4772.
5. F. Liu, S. Wang, C.-L. Gao, Q. Deng, X. Zhu, A. Kostanyan, R. Westerström, F. Jin, S.-Y. Xie, A. A. Popov, T. Greber and S. Yang, Angew. Chem., Int. Ed., 2017, 56, 1830–1834.
6. T. Li, S. Murphy, B. Kiselev, K. S. Bakshi, J. Zhang, A. Eltahir, Y. Zhang, Y. Chen, J. Zhu, R. M. Davis, L. A. Madsen, J. R. Morris, D. R. Karolyi, S. M. Laconte, Z. Sheng and H. C. Dorn, J. Am. Chem. Soc., 2015, 137, 7881–7888.
7. W. Li, F. Qu, L. Liu, Z. Zhang, J. Liang, Y. Lu, J. Zhang, L. Wang, C. Wang and T. Wang, Angew. Chem., Int. Ed., 2022, 61, e202116854.
8. F. Liu, L. Spree, D. S. Krylov, G. Velkos, S. M. Avdoshenko and A. A. Popov, Acc. Chem. Res., 2019, 52, 2981–2993.
9. X. Zhang, W. Li, L. Feng, X. Chen, A. Hansen, S. Grimme, S. Fortier, D. C. Sergentu, T. J. Duignan, J. Autschbach, S. Wang, Y. Wang, G. Velkos, A. A. Popov, N. Aghdassi, S. Duhm, X. Li, J. J. Li, L. Echegoyen, W. H. E. Schwarz and N. Chen, Nat. Commun., 2018, 9, 2753.
10. J. Zhuang, L. Abella, D. C. Sergentu, Y. R. Yao, M. Jin, W. Yang, X. Zhang, X. Li, D. Zhang, Y. Zhao, X. Li, S. Wang, L. Echegoyen, J. Autschbach and N. Chen, J. Am. Chem. Soc., 2019, 141, 20249–20260.
11. Q. Meng, L. Abella, W. Yang, Y. R. Yao, X. Liu, J. Zhuang, X. Li, L. Echegoyen, J. Autschbach and N. Chen, J. Am. Chem. Soc., 2021, 143, 16226–16234.
12. X. Lu, T. Akasaka and S. Nagase, Acc. Chem. Res., 2013, 46, 1627–1635.
13. P. Bagla, Science, 2015, 350, 726–727.
14. T. Abram and S. Ion, Energy Policy, 2008, 36, 4323–4330.
