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### 1 Introduction

Titanium dioxide (TiO<sub>2</sub>) has drawn significant research interest since the last few decades, owing to its intrinsic physicochemical properties and wide range of applications in energy, catalysis, and environmental sciences.<sup>1,2</sup> Molecular analogues of TiO<sub>2</sub> semiconducting materials are Ti–oxo clusters (TOCs), also known as polyoxo–titanium clusters (PTCs).<sup>3–6</sup> PTCs are one of the emerging classes of inorganic metal–oxo nanoparticles. PTCs show photocatalytic activity and find enormous applications in solar energy conversion, degradation of environmental pollutants, wastewater treatment, and other photochemical processes.<sup>7,8</sup> Energy-states and detailed structure–property relationships of PTCs have also been studied in the literature.<sup>9–11</sup> In the recent past, a wide variety of PTCs, such as Ti<sub>6</sub>O<sub>3</sub>,<sup>7</sup> Ti<sub>6</sub>O<sub>4</sub>,<sup>12</sup> Ti<sub>13</sub>O<sub>10</sub>,<sup>13</sup>

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We investigated the gas phase fragmentation events of highly symmetric fullerene-like (FN-like) titanium oxo-cluster anions,  $[H_{12}Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$  (1) and  $[H_7Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$  $(H_2O)_3$ <sup>1-</sup> (2). These oxo-clusters contain a closed cage Ti<sub>42</sub>O<sub>60</sub> core, protected by a specific number of methoxy, methanol, and water molecules acting as ligands. These dianionic and monoanionic species were generated in the gas phase by electrospray ionization of the  $H_6[Ti_{42}(\mu^3-O)_{60}(O^iPr)_{42}(OH)_{12}]$  (TOF) cluster in methanol. Collision induced dissociation studies of 1 revealed that upon increasing the collision energy, the protecting ligands were stripped off first, and  $[Ti_{41}O_{58}]^{2-}$  was formed as the first fragment from the  $Ti_{42}O_{60}$  core. Thereafter, systematic  $TiO_2$  losses were observed giving rise to subsequent fragments like  $[Ti_{40}O_{56}]^{2-}$ ,  $[Ti_{39}O_{54}]^{2-}$ ,  $[Ti_{38}O_{52}]^{2-}$ , etc. Similar fragments were also observed for monoanionic species  $\mathbf{2}$  as well. Systematic 23 TiO<sub>2</sub> losses were observed, which were followed by complete shattering of the cage. We also carried out computational studies using density functional theory (DFT) to investigate the structures and fragmentation mechanism. The fragmentation of TOF was comparable to the fragmentation of  $C_{60}$  ions, where systematic  $C_2$  losses were observed. We believe that this is a consequence of topological similarity. The present study provides valuable insights into the structural constitution of TOF clusters and stability of the parent as well as the resulting cage-fragments in the gas phase.

 $Ti_{17}O_{24}$ ,<sup>14</sup>  $Ti_{18}O_{27}$ ,<sup>15</sup>  $Ti_{25}O_{26}$ ,<sup>16</sup>  $Ti_{28}O_{48}$ ,<sup>17</sup>  $Ti_{34}O_{50}$ ,<sup>18</sup>  $Ti_{52}O_{74}$ ,<sup>14</sup> *etc.*, have been synthesized, by varying O-containing ligands as well as other secondary ligands, with distinct molecular formulae.

Most of the reported PTCs are composed of Ti atoms bonded with O-donor ligands like carboxylates, alkoxides, etc. Apart from O-donor ligands, P-donor ligands like phosphonate, phosphinate and phenyl phosphonate (Phen-PO<sub>3</sub>) as well as N-donor ligands like 2-amino-ethylphosphonate, 1,10-phenanthroline, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), pyridine, etc., exhibit a strong binding affinity with Ti. Fang *et al.* reported  $Ti_{52}(\mu-OH)_2(\mu-O)_{14}(\mu^3-O)_{50}(\mu^4-O)_8$ - $(PA)_{34}(O^{i}Pr)_{28}$  (where PA is propionic acid), which is a PTC with the highest nuclearity reported to date. It consisted of a stepwise layered assembly of smaller units of  $Ti_6(\mu^3-O)_4(BDC)_2(PA)_2(O^iPr)_{10}$ clusters where BDC represents benzenedicarboxylate.14 Other PTCs containing noble metals  $[Ag(CH_3CN)]_2[Ag_6Ti_{16}(\mu_3-O)_{18}(\mu_2 O_4(benzoate)_{26}(CH_3CN)_2$  (PTC-47) and  $[Ag_6Ti_{16}(\mu_3-O)_{16}(\mu_2-$ O)<sub>4</sub>(benzoate)<sub>24</sub>(CH<sub>3</sub>COO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub> (PTC-48) with Ag-O-Ti bonds are also known.<sup>19</sup>

On the other hand, a great variety of fullerene-like (FN-like) inorganic cluster systems with well-established synthetic protocols and structural details have been reported.<sup>20–26</sup> They can be grouped into various classes based on the atomic construction of their metal core, metal–metal bonding, ligands and

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polyoxometalate building units. Several of them contain regular polyhedral cluster-like structures with higher molecular symmetry, like  $As_{20}$  which was reported by Moses *et al.*<sup>20</sup> and  $Mo_{132}O_{372}$  which was reported by Müller *et al.*<sup>26</sup> A sphere-like  $Mo_{72}Fe_{30}$  cluster, with high solution phase stability and pH-dependent tunable size, was reported by Liu *et al.*<sup>27</sup>

Despite the progress in research interest in the bottom-up synthetic strategies and various applications of PTCs, their gas phase behaviours are often unclear. A few Ti–oxo clusters like  $[Ti_{17}(\mu^2-O)_2(\mu^3-O)_{18}(\mu^4-O)_2(PA)_8(O^iPr)_{16}]$ ,<sup>14</sup>  $[Ti_{52}(\mu-OH)_2(\mu-O)_{14}-(\mu^3-O)_{50}(\mu_4-O)_8(PA)_{34}(O^iPr)_{28}]$ ,<sup>14</sup>  $[Eu_{24}Ti_8(L)_{31}(HL)_{42}(CH_3CN)_{11}-(H_2O)_8]\cdot nH_2O$ ,<sup>24</sup>  $(H_2L =$  salicylic acid,  $n \sim 50$ ),  $[Ti_6O_5-(OCH_3)_4(C_5N_3O_2H_7)_4K_2H_5(H_2O)_5]^-$  have been characterized by electrospray ionization mass spectrometry (ESI MS) to understand their composition in the solution phase.<sup>28</sup>

A system of particular importance is titanium-oxofullerene (Ti–oxoFN), Ti<sub>42</sub>O<sub>60</sub>. Gao *et al.* established its crystal structure and revealed its composition as H<sub>6</sub>[Ti<sub>42</sub>( $\mu^3$ -O)<sub>60</sub>(O<sup>i</sup>Pr)<sub>42</sub>(OH)<sub>12</sub>] (TOF), where O<sup>i</sup>Pr is an isopropoxide ligand.<sup>29</sup> This cluster consists of a Ti<sub>42</sub>O<sub>60</sub> core that exhibits an icosahedral (*I*<sub>h</sub>) symmetry, similar to that of C<sub>60</sub>. Facile ionization of the cluster from solution allowed its gas phase characterization by ESI MS. Until now, there have been a few reports on gas phase dissociation studies of small Ti<sub>x</sub>O<sub>y</sub><sup>+</sup> ions, produced by laser ablation Ti in the presence of oxygen, but studies on larger Ti–O clusters, synthesized in the solution or solid phase, remain unexplored.<sup>30,31</sup>

In this paper, we present a study of the gas phase dissociation mechanism of the TOF cluster to understand its structural constitution. We show that upon increasing the collision energy, first, the loss of the peripheral ligands occurred, followed by the dissociation of the metal-oxo cage. TiO<sub>2</sub> units were lost systematically from the Ti-oxo (Ti-O) cage with increasing collision energy (CE) followed by a complete rupture of its structure. This may be compared with the case of fullerenes (FNs), where C2 loss occurred systematically. Thus, gas phase fragmentation events of TOF are shown to have similarities with the gas phase fragmentation of FNs. The dissociation events of TOF were also modelled using density functional theory (DFT) to understand the structures resulting from the fragmentation of the parent  $Ti_{42}O_{60}$ core. We note that understanding advanced materials through mass spectrometry is an important direction of research as demonstrated here.32

### 2 Experimental section

#### 2.1 Reagents and materials

All the reagents were commercially available and were used without further purification. Titanium(v) isopropoxide (Ti(O<sup>i</sup>Pr)<sub>4</sub>, 99.9%, was purchased from Avra Synthesis Private Limited. Analytical grade formic acid (HCOOH), isopropyl alcohol ((CH<sub>3</sub>)<sub>2</sub>CHOH) and HPLC grade toluene and methanol (HOCH<sub>3</sub>) were used.

#### 2.2 Synthesis of TOF

TOF was synthesized by slightly modifying the reported method.  $^{29}$  In  $\sim 5.5$  mL of isopropyl alcohol, 0.92 mL Ti(O<sup>i</sup>Pr)\_4

(3.0 mmol), and 5 drops of formic acid were added at room temperature. The solution was refluxed at 100  $^{\circ}$ C for 4 days and then cooled to room temperature. The solution of the as-synthesized cluster was then slowly evaporated at room temperature. Colourless crystals of TOF were obtained after a few days and used for further studies.

#### 2.3 Instrumentation

UV-Vis studies were performed using a PerkinElmer Lambda 25 UV-vis spectrometer. All ESI MS studies were performed using a Waters Synapt G2-Si high definition mass spectrometer (HDMS). The mass spectrometric measurements were performed in the negative ion mode. For ESI MS studies, TOF was dissolved in a toluene–HOCH<sub>3</sub> mixture at a concentration of  $\sim 1 \,\mu g \, m L^{-1}$ . Capillary voltage, cone voltage, and source offset were kept at 2 kV, 0 V, and 0 V, respectively, to obtain a well resolved mass spectrum of TOF. The source temperature and desolvation temperature were maintained at 100 and 150 °C, respectively. Desolvation gas flow of 400 L  $h^{-1}$  was used. In the Synapt G2-Si instrument, the mass-selected ions pass through trap, ion mobility and transfer cells before entering the time-of-flight analyser. In the trap and transfer cells, the precursor ions can be collided with Ar gas for collision-induced dissociation (CID) studies. In our experiments, we carried out CID in both trap and transfer cells, while the IMS cell was kept off. No extra voltages were applied in the IMS cell to avoid additional fragmentation of the ions. In trap, the collision energy (CE) was varied between 0 and 200 CE (CE is expressed in instrumental units). Further increase of CE was attained by increasing the voltages in the transfer cells. As the IMS cell did not contribute any effect on the applied collision voltages, the total CE is considered as the sum of the trap and transfer CEs. A simplified view of the instrumental set-up is presented in Scheme 1. DFT calculations were performed with the grid-based projector-augmented wave (GPAW) method. All structures were optimized using the Perdew-Burke-Ernzerhof (PBE) functional along with the DZP (double- $\zeta$  plus polarization) basis set in a linear combination of atomic orbitals (LCAO) formalism. Additional details are provided in the ESI<sup>+</sup> (see SI1).

### 3 Results and discussion

The TOF was synthesized following the reported method<sup>29</sup> as described in the experimental section. It was dissolved in toluene and characterized by UV-vis as shown in Fig. S1 (ESI $\dagger$ ). The solution phase absorption spectrum was similar to the reported solid-state UV-vis spectrum.<sup>29</sup> The structure of TOF, modelled using the co-ordinates of its crystal structure,<sup>29</sup> is presented in Fig. 1(A). The metal–oxo core of the cluster consists of 42 Ti atoms, among which 12 Ti atoms, labelled as {Ti1} are seven co-ordinated and the remaining 30 Ti atoms, labelled as {Ti2} are five co-ordinated. These 12 {Ti1} atoms form a platonic {Ti<sub>12</sub>} icosahedron which is further capped by a {Ti<sub>30</sub>} icosidodecahedron. This {Ti<sub>30</sub>} icosidodecahedron is constituted by five co-ordinated Ti atoms {Ti2}. These 42 Ti



Scheme 1 Schematic representation of the instrumental setup used for collision-induced dissociation studies. Collisions occurred in the trap and transfer cells, after mass-selection of the ions using the quadrupole mass filter.



Fig. 1 (A) Molecular structures of TOF, which was modelled using the co-ordinates of its reported crystal structure. Colour codes: Deep blue, {Ti1}; cyan, {Ti2}; red, cage oxygen; blush red, ligand oxygen. (B) ESI MS of TOF. Insets (i) and (ii) show the theoretical and experimental isotopic distributions of the mass spectrum of  $\{H_{12}Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2\}^{2-}$  (1) and  $\{H_7Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_3)^{1-}$  (2), respectively. (C) CID mass spectra of 1. For clarity, the spectra are shown for certain CEs only. (Detailed CID spectra are in Fig. S3 and S4, ESI†). Some of the peaks are labelled as (*x*,*y*) where *x* and *y* correspond to the number of Ti and O atoms of the Ti–O cage fragments, respectively.

atoms are connected by 60  $\mu^3 \cdot O^{2-}$  ions, and the overall structure exhibits a FN-like  $\{O_{60}\}$  arrangement. Specifically, the  $\{O_{60}\}$  cage of the cluster core is comprised of  $\{O_5\}$  pentagonal rings and  $\{O_6\}$  distorted hexagonal rings, arranged in a fashion similar to the  $C_{60}$  cage. The  $\{Ti1\}$  atoms stabilize the 12  $\{O_5\}$  rings of the  $\{O_{60}\}$  cage, giving an overall  $I_h$  symmetry to the cluster, thus establishing its structural analogy with  $C_{60}$ .

ESI MS was performed using a toluene solution of TOF, further diluted with methanol. ESI MS of TOF is presented in Fig. 1(B). The peripheral isopropoxide ligands of TOF were exchanged with methoxy ligands and the cluster was ionized in dianionic and monoanionic states during ESI MS. A similar phenomenon was observed in the reported mass spectrum of TOF also.<sup>29</sup> The compositions of the cluster ions were

confirmed by comparing the experimental isotopic distributions with the calculated ones (Fig. 1(B)(i and ii)). The peaks at m/z 2321 and 4655 were assigned to  $\{H_{12}Ti_{42}O_{60}(OCH_3)_{42}-(HOCH_3)_{10}(H_2O)_2\}^{2-}(1)$  and  $\{H_7Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}-(H_2O)_3\}^{1-}$  (2) ions, respectively. We presumed that the isolated hydrogen atoms  $\{H_{12}\}$  and  $\{H_7\}$  are present at the periphery of cluster ions 1 and 2 respectively but their exact positions are unknown. However, the peaks for these parent cluster ions were also associated with a bunch of other peaks in the m/z range of 2300–2550 and 4525–4800, respectively. Expanded views of these m/z ranges are presented in Fig. S2 (ESI†) which revealed that these peaks originated due to the exchange between isopropoxide and methoxy ligands, occurring in solution.

We primarily focused on CID studies of the doubly charged precursor ion **1**. The precursor ion **1** was selected and collided with Ar gas in the trap and transfer cells. By understanding its fragmentation pathway, we attempted to resolve the structural stability and subunits that constituted the FN-like Ti–O cage.

#### 3.1 CID of TOF

CID is a well-established technique of fragmentation of ions by collision with gas molecules.<sup>33–35</sup> Here, CID of the molecular ion of interest, i.e. (m/z 2321, TOF in 2- charge state) was studied over a range of activation energies, from 2 to 400 CE (Fig. 1(C)). Ion 1 was subjected to collisions with Ar gas inside the trap by gradually increasing energy from 0 to 200 CE. The intensities of the parent and fragmented product ions were monitored carefully. Ion 1 is surrounded by methoxy groups from outside and HOCH<sub>3</sub> and H<sub>2</sub>O ligands from inside the Ti-O cage.<sup>29</sup> With increase in energy from 2 to 20 CE, fragmented ions were seen resulting from the neutral loss of m/z 32. These losses can be attributed to either neutral HOCH<sub>3</sub> loss or loss of a -OCH<sub>3</sub> ligand along with a H. As the -OMe ligands protected the outer surface of the Ti-O cage, whereas the neutral HOCH<sub>3</sub> ligands were confined inside the cage, it is likely that loss of an -OMe ligand along with a H (-OMe/H) will be preferred. As discussed above, these additional Hs are present in the periphery of the ion 1, although their exact positions are unknown. The first two -OCH<sub>3</sub>/H loss resulted in the fragmented ions at m/z 2305 and 2289 (see Fig. S3(C), ESI<sup>+</sup> with molecular formulae  $\{H_{11}Ti_{42}O_{60}(OCH_3)_{41}(HOCH_3)_{10}(H_2O)_2\}^{2-}$  and  $\{H_{10}Ti_{42}O_{60} (OCH_3)_{40}(HOCH_3)_{10}(H_2O)_2\}^{2-}$ , respectively).

With the gradual increase of energy from 20 to 50 CE, two more similar  $-OCH_3/H$  (m/z 32) losses were observed and the subsequent fragmented ions were detected at m/z 2273 and 2257, respectively (see Fig. S3(C), ESI†). With further increase in CE, the intensities of these peaks decreased. After 50 CE, the parent ion 1 was completely converted to fragmented ions and  $\{H_8Ti_{42}O_{60}(OCH_3)_{38}(HOCH_3)_{10}(H_2O)_2\}^{2-}$  appeared as the most abundant species (see Fig. S3(C), ESI†).

At CE 65, the peak for  $\{H_8Ti_{42}O_{60}(OCH_3)_{38}(HOCH_3)_{10}-(H_2O)_2\}^{2-}$  started to fragment and a bunch of peaks of 2– charge state appeared in the *m/z* range of 1580 to 1830 (Fig. S3(A)(iv), ESI<sup>†</sup>). The intensities of these ions increased with increase in CE up to 175 CE (Fig. S3 and S4(i), ESI<sup>†</sup>). With the increase in CE, *m/z* values of the fragment ions moved to

1240–1580. These bunch of peaks appeared with small m/z differences of 7, 8, or 9 between the adjacent peaks. However, these were not well resolved. Also, as the formation of all these ions happened simultaneously, it was difficult to identify any systematic fragmentation here. These mass losses were probably due to the loss of the ligands, OCH<sub>3</sub>, HOCH<sub>3</sub>, and H<sub>2</sub>O occurring simultaneously. Thus, it appeared that in the range of 65 to 175 CE, the ligands of the oxo-cage were lost preferentially.

Above 175 CE, these bunches of doubly charged peaks in the m/z range of 1280–1450 were resolved (see Fig. S4, ESI<sup>+</sup>) and their m/z values and isotopic patterns suggested that at this stage all the ligands of TOF were stripped off. Subsequently, fragmentation of the cage, which contained the Ti<sub>42</sub>O<sub>60</sub> core, was observed in the mass spectrum. In the trap cell, the maximum accelerating voltage could be increased to 200 CE. At CE 200, the fragments observed were  $[Ti_{41}O_{58}]^{2-}$  (*m*/*z* 1445),  $[Ti_{40}O_{56}]^{2-}(m/z \ 1405), [Ti_{39}O_{54}]^{2-}(m/z \ 1365), [Ti_{38}O_{52}]^{2-}(m/z \ 1365)]$ 1325),  $[Ti_{37}O_{50}]^{2-}$  (*m*/*z* 1285) and  $[Ti_{36}O_{48}]^{2-}$  (*m*/*z* 1245) with successive neutral losses of m/z 40, i.e. TiO2 (see Fig. S4, ESI<sup>†</sup>).  $(TiO_2)_n^+$  losses were also observed during photofragmentation or CID of smaller  $Ti_x O_v^+$  clusters, produced by the laser ablation technique in the gas phase.<sup>30,31</sup> All the HOCH<sub>3</sub> and H<sub>2</sub>O ligands, which were confined inside the Ti-O cage, were also lost prior to the formation of the first cage fragment, i.e.  $[Ti_{41}O_{58}]^{2-}$ , see Fig. S3(B) (ESI<sup>†</sup>) and Fig. 1C(v). At 200 CE also, limited fragmentation of the Ti-O core was observed (see Fig. S4(ii), ESI<sup>†</sup>), and it was evident that the Ti-O cage exhibited high gas phase stability and required more energy to undergo complete fragmentation. Further energy required for the fragmentation of the cage was supplied by increasing CE in the transfer cell. In the transfer cells, an additional 0-200 CE was applied. As discussed earlier in the instrumental section, we are referring to the total CE as a sum of the trap and transfer energies. With further increase of CE in the transfer cells, more  $TiO_2$  fragments were lost from the cage. At 300 CE (Fig. 1(C)(iv) and Fig. S4(iv), ESI<sup>†</sup>), fragment ions such as  $[Ti_{35}O_{46}]^{2-}$  (m/z)1205),  $[Ti_{34}O_{44}]^{2-}$  (*m*/*z* 1165),  $[Ti_{33}O_{42}]^{2-}$  (*m*/*z* 1125) and  $[Ti_{32}O_{40}]^{2-}$  (m/z 1085) were observed in ESI MS. All these peaks appeared due to the systematic loss of  $TiO_2$  (Fig. 1(C)(iv and v)) and the fragmentation continued until  $[Ti_{29}O_{34}]^{2-}$  (m/z 965) was formed. Thus, collisional excitation resulted in a systematic loss of TiO<sub>2</sub> subunits, which probably constituted the primary building blocks of the Ti-O cage of TOF. However, after CE 350, again a bunch of poorly resolved peaks appeared in the range below m/z 950 due to further fragmentation of the cage (Fig. 1(C)(v and vi)) which indicated that the cluster core was disrupted completely. The CID mass spectra for the entire range of CEs from 2 to 400 CE are shown in the ESI<sup>+</sup> (Fig. S3 and S4).

However, apart from this fragmentation channel of the ions in the 2– charge state, another pathway of fragmentation from ion 1 was also observed. At 65 CE, a singly charged peak at m/z4530 appeared which was assigned to {H<sub>7</sub>Ti<sub>42</sub>O<sub>60</sub>(OCH<sub>3</sub>)<sub>38</sub>-(HOCH<sub>3</sub>)<sub>10</sub>(H<sub>2</sub>O)<sub>3</sub>}<sup>1–</sup> (see Fig. S3(iv) and S5(A and B), ESI†). A comparison of the isotopic distribution of the theoretical and experimental peaks at m/z 4530 is shown in Fig. S4(C) (ESI†).

With the gradual increase in energy from 65 to 150 CE, a series of singly charged peaks also appeared in the m/z range of 2900-3400 (see Fig. S3(A)(iv-vi), ESI<sup>+</sup>). Similar to the fragment ions in 2- charged state, here also, the bunch of peaks, appearing mostly due to the loss of the peripheral ligands, were not well-resolved until 175 CE. The monoanionic fragment ions,  $[Ti_{41}O_{57}]^{1-}, [Ti_{40}O_{55}]^{1-}, [Ti_{39}O_{53}]^{1-}, [Ti_{38}O_{51}]^{1-}, [Ti_{37}O_{49}]^{1-}$  and  $[Ti_{36}O_{47}]^{1-}$  were detected at 250 CE, which differed by m/z 80 (see Fig. S4(iii), ESI<sup>†</sup>). These were also formed by systematic loss of TiO<sub>2</sub>, similar to the case of the dianionic cage fragments. At around 300 CE, further fragmentation occurred in the monoanionic state too and more TiO2 units were lost from the cage. Thus, the species  $[Ti_{35}O_{45}]^{1-}$ ,  $[Ti_{34}O_{43}]^{1-}$ ,  $[Ti_{33}O_{41}]^{1-}$ and  $[Ti_{32}O_{39}]^{1-}$  were formed at 300 CE (see Fig. S4(iv), ESI<sup>†</sup>). At 400 CE,  $[Ti_{19}O_{13}]^{1-}$  was observed at m/z 1116. The CE could not be increased further in the current instrumental set-up. An expanded view of the CID mass spectrum at 400 CE is shown in Fig. 2, which revealed the presence of another systematic fragmentation pathway for the monoanionic fragmented ions. Each of the above-mentioned monoanionic anions was accompanied by another peak at a slightly lower m/z value with a difference of 16. This was attributed to the loss of an O atom from the respective monoanionic fragments. The molecular compositions of these Ti-O cage fragments were confirmed by comparing the calculated mass spectrum with the experimental ones. Thus, these additional fragment ions were assigned to  $[Ti_{41}O_{56}]^{1-}$ ,  $[Ti_{40}O_{54}]^{1-}$ ,  $[Ti_{39}O_{52}]^{1-}$ ,  $[Ti_{38}O_{50}]^{1-}$ ,  $[Ti_{37}O_{48}]^{1-}$ ,  $[Ti_{36}O_{46}]^{1-}$ ,  $[Ti_{35}O_{44}]^{1-}$ ,  $[Ti_{34}O_{42}]^{1-}$ ,  $[Ti_{33}O_{40}]^{1-}$ ,  $[Ti_{32}O_{38}]^{1-}, [Ti_{31}O_{36}]^{1-}, [Ti_{30}O_{34}]^{1-}, [Ti_{29}O_{32}]^{1-} \text{ and } [Ti_{28}O_{30}]^{1-}$ (see Fig. S6, ESI<sup>†</sup>). In Fig. 2(B), the expanded mass spectrum in

the range of m/z 2448-2485 is shown and theoretical and experimental mass spectrum of [Ti<sub>36</sub>O<sub>46</sub>]<sup>1-</sup> and [Ti<sub>36</sub>O<sub>47</sub>]<sup>1-</sup> are compared. Isotopic distributions of other fragments are shown in the ESI<sup>†</sup> (see Fig. S7). For simplicity, we categorize the fragmentation in the monoanionic charge state into two fragmentation channels: path-I which produced fragment ions containing an odd number of O atoms and path-II which produced fragment ions containing an even number of O atoms. Thus, the systematic loss of neutral TiO<sub>2</sub> was the predominant dissociation pathway of the Ti-O cage in both 2- and 1- charge states. These fragmentation events of the Ti-O cage of TOF are comparable to the dissociation of FN molecules where a systematic loss of C2 units occurred.<sup>36</sup> Similar fragmentation study of the intact monoanionic parent ion 2 (m/z 4655, detected in ESI MS as shown in Fig. 1(B)) was also performed. CID spectra with increasing laboratory CE for 2 are shown in Fig. S8 (ESI<sup>+</sup>). Species 2 also showed a loss of ligands from the cluster with the gradual increase in CE. The fragmentation of species 2 was observed around 400 CE as shown in Fig. S8 and S9 (ESI<sup>†</sup>).

#### 3.2 Collision energy-resolved fragmentation curves

CE resolved fragmentation curves were constructed by plotting the relative intensities of a particular ion as a function of the applied CE.<sup>32,37</sup> The relative intensities of ions were calculated using the following formula:

$$I_{\rm r} = \frac{I_{\rm p}}{I_{\rm t}}$$

where  $I_r$  refers to the relative intensity of a particular ion,  $I_p$  refers to the actual intensity of the particular ion and  $I_t$ 



**Fig. 2** (A) Expanded CID mass spectrum of TOF at 400 CE showing the monoanionic cage fragment ions. Alternative peaks are assigned with (*x*,*y*) where *x* denotes the no. of Ti and *y* denotes the no. of O atoms. Detailed assignments are shown in Fig. S6(B) (ESI<sup>+</sup>). (B) Theoretical and experimental isotopic distributions of one set of fragment ions, *i.e.*  $[Ti_{36}O_{46}]^{1-}$  and  $[Ti_{36}O_{47}]^{1-}$ .

refers to the sum of the intensities of parent and all the fragment ions. CE resolved curves are helpful in understanding the correlation between the yield of the fragment ions and their internal energy distribution.<sup>38,39</sup>

In Fig. 3, CE-resolved dissociation curves for the fragmentation of the dianionic species 1, are presented. Such energyresolved curves explained the extent of energy demand for the dissociation processes and also presented the various parallel and successive fragmentation events of the Ti-O cage as a function of applied CE. CE-resolved curves of the precursor ion 1 and all the mono- and dianionic fragments resulting from it are presented in Fig. 3(A). Fig. 3(A)(i) shows an expanded view of the relative abundance vs. CE of all the above-mentioned fragmented ions. The product ions with relative abundance below 0.01 were neglected in these plots. The curves for the dianionic fragment ions are presented separately in Fig. 3(B). In Fig. 3(C)(i and ii), similar fragmentation curves for the monoanionic anions are shown. The energy-resolved fragmentation curve of the parent dianion 1 exhibited a sigmoidal decay pattern. The intermediate species formed due to the loss of ligands of **1** have been ignored in the energy-resolved studies as those peaks were poor in resolution and also our primary objective was to investigate the fragmentation mechanism of the Ti–O cage. From Fig. 3(A), it is clear that the parent ion **1** was dissociated completely beyond 50 CE. The fragmentation of FN-like cage started around 200 CE, which suggested that though the loss of the peripheral ligands was facile, the Ti–O cage was highly stable in the gas phase and needed high energy to undergo fragmentation. From Fig. 3(B) and (C), it is clear that the loss of TiO<sub>2</sub> occurred in a systematic fashion. In Fig. 3(B), the fragmentation efficiency curves for the dianionic cage fragments of  $[Ti_{34}O_{44}]^{2-}$ ,  $[Ti_{33}O_{42}]^{2-}$ ,  $[Ti_{32}O_{40}]^{2-}$ ,  $[Ti_{31}O_{38}]^{2-}$ ,  $[Ti_{30}O_{36}]^{2-}$  and  $[Ti_{29}O_{34}]^{2-}$  are shown. Fragmentation curves for these selected dianionic fragments alone are shown due to their greater abundance in comparison with other dianionic fragments.

From Fig. 3(B), it appears that the fragments  $[Ti_{34}O_{44}]^{2-}$ ,  $[Ti_{33}O_{42}]^{2-}$ ,  $[Ti_{32}O_{40}]^{2-}$ ,  $[Ti_{31}O_{38}]^{2-}$ , *etc.* were produced simultaneously. This may be due to the fact that for a given CE, there will be a broad internal energy distribution leading to different fragmentation outcomes. Initially, these ions increased in



**Fig. 3** Collision energy-resolved relative abundances of parent and fragment ions of **1** as a function of collision energy (CE). (A) Relative abundance vs. CE plot of the precursor ion **1**, and anionic Ti–O cage fragment units are shown. In the inset (A)(i), expanded views of curves for the fragment ions in the range of 200–400 CE. (B) Relative abundance vs. CE plot of dianionic fragment ions,  $[Ti_{34}O_{44}]^{2-}$ ,  $[Ti_{32}O_{40}]^{2-}$ ,  $[Ti_{31}O_{36}]^{2-}$ ,  $[Ti_{30}O_{36}]^{2-}$  and  $[Ti_{29}O_{34}]^{2-}$ . (C) (i) and (ii) show the relative abundance vs. CE plots for monoanionic cage fragment ions of paths I and II.

intensity and after reaching a threshold energy, they started to undergo further fragmentation. The ions  $[Ti_{34}O_{44}]^{2-}$ ,  $[Ti_{33}O_{42}]^{2-}$ ,  $[Ti_{32}O_{40}]^{2-}$ ,  $[Ti_{31}O_{38}]^{2-}$ ,  $[Ti_{30}O_{36}]^{2-}$  and  $[Ti_{29}O_{34}]^{2-}$  started dissociating after 320, 325, 330, 345, 352 and 367 CE, respectively, as observed from Fig. 3(B). Thus, the energy required for dissociation of each of these fragment ions was different suggesting a change in the inherent stability of the cage after systematic TiO<sub>2</sub> loss.

Similar graphs of monoanionic fragments produced from precursor **1** are presented in Fig. 3(C). The CE resolved graphs for the ions  $[Ti_{41}O_{57}]^{1-}$ ,  $[Ti_{40}O_{55}]^{1-}$ ,  $[Ti_{39}O_{53}]^{1-}$ ,  $[Ti_{38}O_{51}]^{1-}$ ,  $[Ti_{37}O_{49}]^{1-}$ ,  $[Ti_{36}O_{47}]^{1-}$  and  $[Ti_{35}O_{45}]^{1-}$  formed by path-I (see Fig. 3(C)(i)) and  $[Ti_{41}O_{56}]^{1-}$ ,  $[Ti_{40}O_{54}]^{1-}$ ,  $[Ti_{39}O_{52}]^{1-}$ ,  $[Ti_{38}O_{50}]^{1-}$ ,  $[Ti_{37}O_{48}]^{1-}$ ,  $[Ti_{36}O_{46}]^{1-}$  and  $[Ti_{35}O_{44}]^{1-}$  formed by path-II (see Fig. 3(C)(ii)), showed a similar trend of fragmentation to the dianionic species. The yield of ions beyond 400 CE was not monitored. Thus, it was clear that the systematic loss of TiO<sub>2</sub> was observed from the Ti–O cage and the fragments obtained in the subsequent stages exhibited different internal energy distribution. A sequential fragmentation mechanism of **1** is proposed in Fig. 4 based on the detection of CID mass spectra and nature of CE resolved curves of fragment ions.

The fragmentation events of the Ti–O FN cage,  $\{Ti_{42}O_{60}\}$ , of (1) can be correlated with the fragmentation events of carbon FNs.<sup>40,41</sup> The simplified stepwise dissociation scheme of the FN-like cage of TOF is shown in Scheme 2, which ultimately dissociated into Ti–O fragments. Electron impact ionization (EI)

and higher energy (8 keV) CID/mass-analysed ion kinetic energy spectra of C<sub>60</sub><sup>+</sup> (*m*/*z* 720) under single collision condition was reported and the fragmentation process resulted in corresponding losses of C<sub>2</sub> molecules, yielding smaller even-numbered carbon cluster fragment ions.<sup>40,42,43</sup> Fragmentation of various FNs and sequential C<sub>2</sub> loss mechanisms were also studied by low- and high-energy CID and surface impact at different energies.<sup>44</sup> Likewise, fast-atom bombardment (FAB) of multicharged C<sub>60</sub><sup>z+</sup> (*z* = 1–4) with He also resulted in multicharged fragment ions by neutral losses of C<sub>2</sub>.<sup>45,46</sup> There are several such mass spectrometric reports.<sup>47–49</sup> Thus, the dissociation mechanism of the Ti–O cage and carbon FNs are comparable.

#### 3.3 Computational study

We have modelled the structure of the parent ion  $[H_{12}Ti_{42}-O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$  (1) based on the reported crystal structure of TOF,<sup>29</sup>  $[H_6[Ti_{42}(\mu^3-O)_{60}(O^iPr)_{42}(OH)_{12}]]$  and optimized the structure of 1 and that of its major fragments using DFT (details of methods are in the experimental section). In the structure of 1, for simplicity, we neglected all the 12 hydrogens  $(H_{12})$  as their precise positions are unknown from experiment. However, we continue to write the number of extra hydrogens associated with the cluster in the structural formula for clarity, even though they are not included in our structural models.



Fig. 4 Fragmentation pathways of targeted molecular ion  $\mathbf{1}$ ; a ( $0 \le a < 38$ ), b (0 < b < 10), and c ( $0 \le c < 3$ ) labels in molecular formulae represent the losses of OCH<sub>3</sub>, HOCH<sub>3</sub>, H<sub>2</sub>O ligands, respectively in the fragmentation process.



In the first step, all the peripheral ligands, *i.e.*, the forty-two isopropyl groups of TOF, were exchanged with methyl groups (-CH<sub>3</sub>) and the preliminary structure of H<sub>6</sub>[Ti<sub>42</sub>O<sub>60</sub>(O-CH<sub>3</sub>)<sub>42</sub>(OH)<sub>12</sub>] was optimized (see in Fig. S9 and Table S1, ESI†). The charge state of [Ti<sub>42</sub>O<sub>60</sub>(OCH<sub>3</sub>)<sub>42</sub>(OH)<sub>12</sub>] is -6 with no extra hydrogens. Here, the hydrogens are weakly interacting with the cluster unit in the crystalline phase and would not be involved in charge transfer.

In the second step, we made internal ligand substitutions by replacing ten of the -OH groups by ten -(OH)CH3 groups and the remaining two -OH groups were replaced by two H<sub>2</sub>Ogroups to give an initial geometry of 1 which we attempted to optimize in the -2 charge state. In the course of DFT optimization of 1, we found that convergence could not be obtained, and we then repeated the optimization by increasing the total charge in units of one starting from -6 to +6, and out of all of these charge states, the DFT calculation converged only in the +4 charge state. In DFT calculations, there is a longstanding charge-delocalization issue and electronic states tend to be more delocalized than found experimentally.<sup>50</sup> As a result, charges from DFT calculations generally do not reproduce numerically the oxidation numbers of atoms, but the geometries from DFT simulations can often reproduce the structure and bonding configurations of molecules and materials in those oxidation states.

The positive charge could be qualitatively understood if we assume that the twelve hydrogen atoms donate electrons as ligands to clusters **1** and **2** so that in their absence, the clusters are effectively more positively charged. For clusters **1** and **2** in the gas phase, the surface hydrogen atoms may be more closely bound and could donate electrons to the cluster. Therefore, the charge of -2 observed in the mass spectrum for **1** is more negative than in the deprotonated state used in DFT calculations with a charge of +4. The resulting optimized structure of  $[Ti_{42}O_{60}(OCH_3)_{42}(OHCH_3)_{10}(H_2O)_2]^{4+}$  is equivalent to that of  $[H_{12}Ti_{42}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$  as shown in Fig. 5(A)(a).

The optimized structure of **1** and its charge state calculation including the constituent species such as  ${Ti1}O_7$ ,  ${Ti2}O_5$ , OCH<sub>3</sub>, (HO)CH<sub>3</sub>, H<sub>2</sub>O are shown in Fig. S10 and in SI2 (ESI<sup>†</sup>),

respectively. Note that {Ti1} and {Ti2} refer to distinct coordination types of Ti atoms in the structure. For the methanol ligands, we observed an average  ${Ti1}-HO(CH_3)$  bond larger by 0.3 Å (15%) compared to the {Ti1}-OH bond distance found in  $[Ti_{42}O_{60}(OCH_3)_{42}(OH)_{12}]^{6-}$ , indicating only weak covalent Ti-O bonds with methanol. Furthermore, the two -OH<sub>2</sub> groups are completely detached from {Ti1} sites as two separate water molecules with non-covalent {Ti1}-O bonding distances of 2.53 Å and 2.60 Å, with the variation being dependent on the space available near the particular water moiety. The separation of methanol and water molecules from {Ti1} sites within the cage leaves the total structure with more cationic charges. Thus, the weakly bound methanol and free water molecules are confined in a highly cationic charged cage because fewer electrons are donated by these ligand groups compared to OH groups, which are closely bound to the cage.

On the other hand, it was observed that the bonding interaction of the peripheral methoxide ligands attached to seven-coordinated {Ti1} atoms was greatly strengthened as indicated by the contraction in the {Ti1}-O bond distance by 0.15 Å (6.3%). Similarly, it was noticed that the interaction of methoxide ligands bonded to the five-coordinated {Ti2} atoms were also strengthened as shown by a bond contraction of 0.11 Å (5.9%).

While the overall charge of TOF can be obtained using a standard organometallic electron counting procedure (see Table S1, ESI<sup>†</sup>), we found that application of simplistic electron counting to cluster ion 1 did not yield the correct charge state, which may be attributed to partial charge transfer. To better understand the partial charge transfer processes which stabilize cluster 1, Bader charge analysis of structure 1 was carried out (see in Tables S2–S4, ESI<sup>†</sup>). The average charge of ten methanol molecules was  $-0.028e^-$  and that of the two water molecules was  $-0.006e^-$ . This analysis indicated that there is no significant charge transfer from caged methanol and water molecules to the seven-coordinated {Ti1} centres. Thus, the molecules may be considered free in the sense that they are subject only to supramolecular interactions. As a result of this, the {Ti1} atoms have stronger interaction with the methoxide



**Fig. 5** (A) The DFT-optimized structures of (a)  $[H_{12}T_{142}O_{60}(OCH_3)_{42}(HOCH_3)_{10}(H_2O)_2]^{2-}$ , (b)  $[H_{12}T_{142}O_{60}(OHCH_3)_{10}(H_2O)_2]^{2-}$ , (c)  $[T_{141}O_{58}(HOCH_3)]^{2-}$  and (d)  $[T_{141}O_{58}]^{2-}$ . (B) Comparison between free energy changes of cages (i and ii) due to loss of TiO<sub>2</sub> with {Ti1} (deep blue colour) and {Ti2} (light blue colour) sites. Colour of oxygen, carbon, and hydrogen atoms are red, dark grey and grey respectively). The twelve hydrogen atoms have been not included in the structures as described in the text.

ligands, since the DFT-optimized structure for cluster 1 compared to TOF shows the reduction of the average  ${Ti1}-O(CH_3)$ bond length from 1.90 to 1.8 Å, and a more positive average charge on the methoxide ligands bonded to {Ti1} centre  $(-0.37e^{-})$ , compared to  $\{Ti2\}$  centres  $(-0.42e^{-})$ . These results suggest the possibility of greater electron donation (loss of negative charge) from methoxide ligands to {Ti1} centres in cluster 1. DFT study of average charges on OCH<sub>3</sub> ligands in TOF indicates a slightly more positive value  $(-0.56e^{-})$  at  $\{Ti1\}$ centres in TOF  $(-0.56e^{-})$  compared to that at {Ti2} centres  $(-0.57e^{-})$ , which supports our finding of greater partial charge transfer from OCH<sub>3</sub> ligands at {Ti1} centers compared to {Ti2} centers in cluster 1. This increase in partial charge transfer may contribute to stabilizing the {Ti1}-centres when molecules are free in the cage. Such charge transfer differences at different {Ti1} sites may be understood as polarization effects on the Ti-O(CH<sub>3</sub>) bond caused by the methanol and water molecules inside the cage as shown in Fig. S11 (ESI<sup>†</sup>). The strength of this effect would be stronger for methanol molecules than water molecules due their closer position to the {Ti1} centre. Furthermore, since the polarization effect is not present for {Ti2} centres, they attract less charge from the methoxide ligands. In reality, the cluster **1** may also be further stabilized *via* charge transfer with the hydrogen ions.

We computationally investigated all the intermediate stages of the cluster fragmentation as observed in the experiments such as loss of peripheral ligands, cleavage of the Ti-O cage, release of the ligands from inside the cage and finally the fragmentation of the Ti-O cage in detail. The structures of the major ions identified in MS such as the parent ion and major fragmented product ions were optimized and stacked as shown in Fig. 5. The structure of 1 was optimized after removing twelve peripheral -OCH3 ligand groups from {Ti1} sites (see Fig. S12(A), ESI<sup>†</sup>). However, the Ti-O bonding interaction at {Ti1} sites along the wall of the cage underwent a significant bond elongation up to 4.4% and {Ti2}-O bonding reorganization at {Ti2} sites led to {Ti2}-O bond distances increase on average by 1.3%. The local geometry around {Ti1} atoms become more distorted with different bond lengths for different neighbouring bridging O atoms. The bond strains due to the {Ti1} attraction to the methanolic O atoms. The {Ti2}-O pentagonal bonding geometry remained unaltered due to the removal of

twelve OCH<sub>3</sub> ligand groups, since there are no strong internal bonding interactions for {Ti2} compared to {Ti1} atoms. These observations may be explained by the higher bond strain at {Ti1} sites compared to {Ti2} sites. Theoretically optimized structures of intermediates  $[H_{12}Ti_{42}O_{60}(CH_3O)_{30}(CH_3OH)_{10}(H_2O)_2]^{2-}$  and  $[H_{12}Ti_{41}O_{58}(CH_3OH)_{10}(H_2O)_2]^{2-}$  formed during gas phase fragmentation are shown in Fig. S13 (ESI<sup>†</sup>).

In the second intermediate structure shown in Fig. 5(A)(b)), all the remaining thirty  $-OCH_3$  peripheral ligands were lost from {Ti2} sites and the bonding interaction of Ti–O were seen to have strengthened in the cage and the local geometry around Ti became asymmetric. To understand the preferential site for TiO<sub>2</sub> fragment loss, first, we removed fragments containing {Ti1} and {Ti2} atoms from the surface of the methoxy ligandfree cluster. The cage fragment structures were optimized after removing one TiO<sub>2</sub> unit each attached to the {Ti1} and {Ti2} sites and they are shown in Fig. 5(B)(i and ii), respectively. Based on the relative ordering of the total energies of the two different open cage shell structures, it was confirmed that TiO<sub>2</sub> removal from a {Ti1} site is energetically favourable than from a {Ti2} site.

It is interesting to observe that the total energy of the structure with a  $\{Ti1\}O_2$  unit loss in Fig. 5B(i) is 3.95 eV lower than the total energy of the structure with a {Ti2}O<sub>2</sub> unit loss of Fig. 5B(ii). This relative energetic ordering,  $E({Ti1}O_2 \text{ loss}) <$  $E({\text{Ti2}}O_2 \text{ loss})$ , is due to the increased bond strain around  ${\text{Ti1}}$ atoms compared to that around {Ti2} atoms, as discussed earlier. Therefore, a {Ti1}O2 unit loss leads to a greater structural relaxation, as the potential energy stored in the strained bonds is released. Moreover, in the {Ti1}O2 removed structure, i.e., Fig. 5B(i), a new bond appears between a {Ti2} atom on the edge of the cage opening and the O atom of the methanol which had been previously bonded to the  $\{Ti1\}$  atom of the lost  $\{Ti1\}O_2$  unit. During structural relaxation, this methanol unit rotates from the inside to the outside of the cage while being anchored to the {Ti2} atom which protrudes like a lip to the cage opening as seen in Fig. 5B(i). However, such stabilization by methanol rotating out of the cage while being hinged is not possible in the case of  $\{Ti2\}O_2$ , which leaves behind six-coordinated {Ti1} atoms that are more rigid and the methanol units remain tightly bonded inside the cage. There could be additional weak interactions arising from hydrogen bonds contributing to these.

The opening of cage with TiO<sub>2</sub> loss at {Ti1} sites left a hole with dimensions of ~7.2 Å × 7.0 Å and the edges of the opening were puckered due to {Ti2} atoms interacting with methanol. In contrast, for the cage opening with TiO<sub>2</sub> loss from {Ti2} sites, it was noted that the opening remained unaltered during optimization apart from a slight contraction of the cage opening after the complete removal of ligands from the cage. Loss of all ligands makes  $[Ti_{41}O_{58}]^{2-}$  and subsequent fragmentation is expected from this cluster.

### 4 Conclusions

We performed detailed CID studies on a Ti–oxo cluster protected by ligands, referred to as TOF. Upon increasing the CE, after the ligands were stripped off, a systematic loss of TiO<sub>2</sub> was observed during the fragmentation of the FN-like cluster core. Firstly, all the peripheral ligands along with the ligands inside the cluster-core were lost from TOF leading to the formation of  $[Ti_{41}O_{58}]^{2-}$ . From this species, up to 23 systematic TiO<sub>2</sub> losses were observed, and finally  $[Ti_{19}O_{13}]^{1-}$  was formed. Beyond this stage, upon further increase of energy, the structure collapsed completely. The fragmentation pathway was comparable to that of C<sub>60</sub> and the other FNs where systematic C<sub>2</sub> losses were seen up to C<sub>30</sub><sup>+</sup>, which was followed by shattering of the cage.<sup>51-53</sup> Expanding such studies to other metal oxoFNs<sup>26,27,54-57</sup> would provide greater insights into the science of such structures.

### Author contributions

T. P. proposed the project. J. R. and P. C. performed the experiments. J. R. prepared the samples. J. R. and P. C. performed mass spectrometric measurements. G. P. and G. N. carried out theoretical calculations. J. R. and P. C. wrote the first draft of the manuscript, and the final version of the manuscript was prepared through the contributions of all authors. All authors have given approval to the final version of the manuscript.

### Conflicts of interest

There are no conflicts to declare.

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### References

- 1 A. Kubacka, M. Fern Andez-García and G. Col, Advanced Nanoarchitectures for Solar Photocatalytic Applications, *Chem. Rev.*, 2012, **112**, 1555–1614.
- 2 Y. Gao, W. Nie, Q. Zhu, X. Wang, S. Wang, F. Fan and C. Li, The Polarization Effect in Surface-Plasmon-Induced Photocatalysis on Au/TiO<sub>2</sub> Nanoparticles, *Angew. Chem.*, 2020, 132, 18375–18380.
- 3 C. Wang, C. Liu, L. Jiao Li and Z.-M. Sun, Synthesis, Crystal Structures, and Photochemical Properties of a Family of Heterometallic Titanium Oxo Clusters, *Inorg. Chem.*, 2019, **58**, 6312–6319.
- 4 S. Chen, W.-H. Fang, L. Zhang and J. Zhang, Atomically Precise Multimetallic Semiconductive Nanoclusters with Optical Limiting Effects, *Angew. Chem., Int. Ed.*, 2018, 57, 11252–11256.

- 5 L. Rozes and C. Sanchez, Titanium oxo-clusters: Precursors for a Lego-like construction of nanostructured hybrid materials, *Chem. Soc. Rev.*, 2011, **40**, 1006–1030.
- 6 P. Coppens, Y. Chen and E. Trzop, Crystallography and Properties of Polyoxotitanate Nanoclusters, *Chem. Rev.*, 2014, 114, 9645–9661.
- 7 W.-H. Fang, L. Zhang and J. Zhang, Synthetic strategies, diverse structures and tuneable properties of polyoxotitanium clusters, *Chem. Soc. Rev.*, 2018, 47, 404–421.
- 8 R. Chen, Z.-F. Hong, Y.-R. Zhao, H. Zheng, G.-J. Li, Q.-C. Zhang, X.-J. Kong, L.-S. Long and L.-S. Zheng, Ligand-Dependent Luminescence Properties of Lanthanide–Titanium Oxo Clusters, *Inorg. Chem.*, 2019, 58, 15008–15012.
- 9 X. Fan, J. Wang, K. Wu, L. Zhang and J. Zhang, Isomerism in Titanium-Oxo Clusters: Molecular Anatase Model with Atomic Structure and Improved Photocatalytic Activity, *Angew. Chem., Int. Ed.*, 2019, **58**, 1320–1323.
- 10 Y.-Z. Yu, Y.-R. Zhang, C.-H. Geng, L. Sun, Y. Guo, Y.-R. Feng, Y.-X. Wang and X.-M. Zhang, Precise and Wide-Ranged Band-Gap Tuning of Ti6-Core-Based Titanium Oxo Clusters by the Type and Number of Chromophore Ligands, *Inorg. Chem.*, 2019, **58**, 16785–16791.
- 11 S. Pike, T. Krämer and F. Tuna, Photo-redox reactivity of titanium-oxo clusters: Mechanistic insight into a two-electron intramolecular process, and structural characterisation of mixed-valent Ti(III)/Ti(IV) products, *Chem. Sci.*, 2019, **10**, 6886–6898.
- 12 M. Czakler, C. Artner and U. Schubert, Two new hexanuclear titanium oxo cluster types and their structural connection to known clusters, *New J. Chem.*, 2018, **42**, 12098–12103.
- 13 J. Le Hou, W. Luo, Y. Y. Wu, H. C. Su, G. L. Zhang, Q. Y. Zhu and J. Dai, Two Ti13-oxo-clusters showing non-compact structures, film electrode preparation and photocurrent properties, *Dalton Trans.*, 2015, 44, 19829–19835.
- 14 W.-H. Fang, L. Zhang and J. Zhang, A 3.6 nm Ti52–Oxo Nanocluster with Precise Atomic Structure, *J. Am. Chem. Soc.*, 2016, **138**, 7480–7483.
- 15 G. Zhang, C. Liu, D.-L. Long, L. Cronin, C.-H. Tung and Y. Wang, Water-Soluble Pentagonal-Prismatic Titanium-Oxo Clusters, J. Am. Chem. Soc., 2016, 138, 11097–11100.
- 16 Y. Chen, E. Trzop, J. D. Sokolow and P. Coppens, Direct Observation of the Binding Mode of the Phosphonate Anchor to Nanosized Polyoxotitanate Clusters, *Chem. – Eur. J.*, 2013, **19**, 16651–16655.
- 17 N. Narayanam, W.-H. Fang, K. Chintakrinda, L. Zhang and J. Zhang, Deep eutectic-solvothermal synthesis of titaniumoxo clusters protected by  $\pi$ -conjugated chromophores, *Chem. Commun.*, 2017, **53**, 8078–8080.
- 18 J. D. Sokolow, E. Trzop, Y. Chen, J. Tang, L. J. Allen, R. H. Crabtree, J. B. Benedict and P. Coppens, Binding modes of carboxylate- and acetylacetonate-linked chromophores to homodisperse polyoxotitanate nanoclusters, *J. Am. Chem. Soc.*, 2012, **134**, 11695–11700.
- 19 S. Chen, W. H. Fang, L. Zhang and J. Zhang, Atomically Precise Multimetallic Semiconductive Nanoclusters with Optical Limiting Effects, Angew. Chem., Int. Ed., 2018, 57, 11252–11256.

- 20 M. J. Moses, J. C. Fettinger and B. W. Eichhorn, Interpenetrating As20 fullerene and Ni12 icosahedra in the onionskin  $[As@Ni_{12}@As_{20}]^{3-}$  ion, *Science*, 2003, **300**, 778–780.
- 21 T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria and R. E. Smalley, Uranium Stabilization of C28: A Tetravalent Fullerene, *Science*, 1992, 257, 1661–1664.
- 22 L. Qin, G.-J. Zhou, Y.-Z. Yu, H. Nojiri, C. Schröder, R. E. P. Winpenny and Y.-Z. Zheng, Topological Self-Assembly of Highly Symmetric Lanthanide Clusters: A Magnetic Study of Exchange-Coupling "Fingerprints" in Giant Gadolinium(m) Cages, *J. Am. Chem. Soc.*, 2017, **139**, 16405–16411.
- 23 S.-T. Zheng and G.-Y. Yang, Recent advances in paramagnetic-TM-substituted polyoxometalates (TM = Mn, Fe, Co, Ni, Cu), *Chem. Soc. Rev.*, 2012, 41, 7623–7646.
- 24 H. Zheng, M.-H. Du, S.-C. Lin, Z.-C. Tang, X.-J. Kong, L.-S. Long and L.-S. Zheng, Assembly of a Wheel-Like Eu24Ti8 Cluster under the Guidance of High-Resolution Electrospray Ionization Mass Spectrometry, *Angew. Chem., Int. Ed.*, 2018, 57, 10976–10979.
- 25 X.-J. Kong, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, Keeping the Ball Rolling: Fullerene-like Molecular Clusters, *Acc. Chem. Res.*, 2009, 43, 201–209.
- 26 R. W. Pow, W. Xuan, D.-L. Long, N. L. Bell and L. Cronin, Embedding alkenes within an icosahedral inorganic fullerene {(NH<sub>4</sub>)<sub>42</sub>[Mo<sub>132</sub>O<sub>372</sub>(L)30(H<sub>2</sub>O)72]} for trapping volatile organics, *Chem. Sci.*, 2020, **11**, 2388–2393.
- 27 T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen and A. Müller, Deprotonations and Charges of Well-Defined {Mo<sub>72</sub>Fe<sub>30</sub>} Nanoacids Simply Stepwise Tuned by pH Allow Control/Variation of Related Self-Assembly Processes, *J. Am. Chem. Soc.*, 2006, **128**, 15914–15920.
- 28 S. S. Passadis, S. Hadjithoma, A. G. Kalampounias, A. C. Tsipis, S. Sproules, H. N. Miras, A. D. Keramidas and T. A. Kabanos, Synthesis, structural and physicochemical characterization of a new type Ti6-oxo cluster protected by a cyclic imide dioxime ligand, *Dalton Trans.*, 2019, 48, 5551–5559.
- 29 M.-Y. Gao, F. Wang, Z.-G. Gu, D.-X. Zhang, L. Zhang and J. Zhang, Fullerene-like Polyoxotitanium Cage with High Solution Stability, J. Am. Chem. Soc., 2016, 138, 2556–2559.
- 30 M. Jadraque, B. Sierra, A. Sfounis and M. Velegrakis, Photofragmentation of mass-selected titanium oxide cluster cations, *Appl. Phys. B: Lasers Opt.*, 2010, **100**, 587–590.
- 31 M. Velegrakis, M. Massaouti and M. Jadraque, Collisioninduced dissociation studies on gas-phase titanium oxide cluster cations, *Appl. Phys. A: Mater. Sci. Process.*, 2012, 108, 127–131.
- 32 P. Chakraborty, A. Baksi, E. Khatun, A. Nag, A. Ghosh and T. Pradeep, Dissociation of Gas Phase Ions of Atomically Precise Silver Clusters Reflects Their Solution Phase Stability, *J. Phys. Chem. C*, 2017, **121**, 10971–10981.
- 33 M. T. Rodgers and P. B. Armentrout, *Comprehensive Coordination Chemistry II*, Elsevier Ltd, 2004, vol. 2, pp. 141–158.
- 34 S. A. McLuckey, Principles of collisional activation in analytical mass spectrometry, J. Am. Soc. Mass Spectrom., 1992, 3, 599–614.

- 35 A. G. Harrison, Energy-resolved mass spectrometry: a comparison of quadrupole cell and cone-voltage collision-induced dissociation, *Rapid Commun. Mass Spectrom.*, 1999, 13, 1663–1670.
- 36 F. Lépine, B. Climen, M. A. Lebeault and C. Bordas, Time-dependent delayed electron spectra: A direct measurement of total decay rate as a function of internal energy, *Eur. Phys. J. D*, 2009, 55, 627–635.
- 37 R. W. Kirschbaum, M. Hausmann, O. V. Boltalina, S. H. Strauss and T. Drewello, Energy-dependent gas-phase fragmentation of fluorofullerene multiply charged anions (MCAs), *Phys. Chem. Chem. Phys.*, 2015, **17**, 23052–23058.
- 38 J. S. Klassen and P. Kebarle, Collision-Induced Dissociation Threshold Energies of Protonated Glycine, Glycinamide, and Some Related Small Peptides and Peptide Amino Amides, J. Am. Chem. Soc., 1997, 119, 6552–6563.
- 39 A. Kafle, C. Nwokolo, L. Sanchez and P. B. Armentrout, Threshold Collision-Induced Dissociation of Hydrated Thorium(IV) Trihydroxide Cation: Experimental and Theoretical Investigation of the Binding Energies for Th(OH)<sub>3</sub> + (H<sub>2</sub>O)*n* Complexes (n = 1-4), *J. Phys. Chem. A*, 2020, 124, 3090–3100.
- 40 I. N. Ioffe, O. N. Mazaleva, L. N. Sidorov, S. Yang, T. Wei, E. Kemnitz and S. I. Troyanov, Cage Shrinkage of Fullerene via a C<sub>2</sub> Loss: from IPR C<sub>90</sub>(28)Cl<sub>24</sub> to Nonclassical, Heptagon-Containing C<sub>88</sub>Cl<sub>22/24</sub>, *Inorg. Chem.*, 2013, **52**, 13821–13823.
- 41 H. Shen, P. Hvelplund, D. Mathur, A. Bárány, H. Cederquist, N. Selberg and D. C. Lorents, Fullerene-fullerene collisions: Fragmentation and electron capture, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1995, 52, 3847–3851.
- 42 E. E. B. Campbell, T. Raz and R. D. Levine, Internal energy dependence of the fragmentation patterns of  $C_{60}$  and  $C_{60}^{+}$ , *Chem. Phys. Lett.*, 1996, **253**, 261–267.
- 43 T. Pradeep and R. G. Cooks, C<sub>60</sub> inflation: production of C<sub>62</sub>, C<sub>64</sub>, ..., Int. J. Mass Spectrom. Ion Process., 1994, 135, 243-247.
- 44 R. D. Beck, J. Rockenberger, P. Weis and M. M. Kappes, Fragmentation of  $C_{60}^+$  and higher fullerenes by surface impact, *J. Chem. Phys.*, 1996, **104**, 3638–3650.
- 45 J. H. Gross, S. Giesa and W. Krätschmer, Negative-ion lowtemperature fast-atom bombardment mass spectrometry of

monomeric and dimeric [60]fullerene compounds, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 815–820.

- 46 R. J. Doyle and M. M. Ross, Dissociations of singly and multiply charged fullerene ions, *J. Phys. Chem.*, 2002, 95, 4954–4956.
- 47 V. Y. Markov, A. Y. Borschevsky and L. N. Sidorov, MALDI mass spectrometry of fullerene derivatives, *Int. J. Mass Spectrom.*, 2012, **325–327**, 100–112.
- 48 G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, Open-cage fullerenes: Towards the construction of nanosized molecular containers, *Chem. Soc. Rev.*, 2010, **39**, 817–844.
- 49 H. Zettergren, Interactions of energetic ions with fullerenes, PAHs, and their weakly bound clusters, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms*, 2017, 408, 9–15.
- 50 A. J. Cohen, P. Mori-Sánchez and W. Yang, Insights into current limitations of density functional theory, *Science*, 2008, **321**, 792–794.
- 51 D. R. Luffer and K. H. Schram, Electron ionization mass spectrometry of synthetic C<sub>60</sub>, *Rapid Commun. Mass Spectrom.*, 1990, 4, 552–556.
- 52 K. Hata, M. Ariff, K. Tohji and Y. Saito, Selective formation of C20 cluster ions by field evaporation from carbon nanotubes, *Chem. Phys. Lett.*, 1999, **308**, 343–346.
- 53 R. Ehlich, P. Landenberger and H. Prinzbach, Coalescence of C20 fullerenes, J. Chem. Phys., 2001, 115, 5830–5835.
- 54 D. Schröder, Applications of Electrospray Ionization Mass Spectrometry in Mechanistic Studies and Catalysis Research, *Acc. Chem. Res.*, 2012, **45**, 1521–1532.
- 55 L. Suber, M. Bonamico and V. Fares, Synthesis, Magnetism, and X-ray Molecular Structure of the Mixed-Valence Vanadium(v/v)–Oxygen Cluster [VO<sub>4</sub>  $\subset$  (V<sub>18</sub>O<sub>45</sub>)]9-, *Inorg. Chem.*, 1997, **36**, 2030–2033.
- 56 H. Zheng, M.-H. Du, S.-C. Lin, Z.-C. Tang, X.-J. Kong, L.-S. Long and L.-S. Zheng, Assembly of a Wheel-Like Eu 24 Ti 8 Cluster under the Guidance of High-Resolution Electrospray Ionization Mass Spectrometry, *Angew. Chem., Int. Ed.*, 2018, 57, 10976–10979.
- 57 J. Lin, N. Li, S. Yang, M. Jia, J. Liu, X.-M. Li, L. An, Q. Tian, L.-Z. Dong and Y.-Q. Lan, Self-Assembly of Giant Mo<sub>240</sub> Hollow Opening Dodecahedra, *J. Am. Chem. Soc.*, 2020, 142, 13982–13988.