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Introduction 1.

It is well known in chemistry that boron has a strong propensity to form delocalized multi-center-two-electron (mc-2e) bonds in both bulk allotropes and polyhedral molecules due to its prototypical electron deficiency.^{1,2} Combined photoelectron spectroscopy (PES) and first-principles theory investigations in the past two decades have unveiled a rich landscape for size-selected boron clusters $(B_n^{-/0})$ from planar or quasiplanar structures (n = 3-38) to cage-like borospherenes (n = 39, 40) characterized with both delocalized σ and π bonds.³⁻⁷ Seashell-like B_{28}^{-} and B_{29}^{-} , the smallest borospherenes, were recently observed in PES measurements as minor isomers.8,9 Joint ion-mobility experiments and density functional theory investigations, on the other hand, indicated that monocationic boron clusters B_n^+ possess double-ring (DR) tubular structures in the size range of n = 16-25,¹⁰ unveiling another important structural domain in boron nanoclusters. An almost perfect DR tubular B_{20} was predicted to be the global minimum (GM)

Predicting lanthanide boride inverse sandwich tubular molecular rotors with the smallest core-shell structure*

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Lanthanide-boron binary clusters possess interesting structures and bonding which may provide insights into designing new boride nanomaterials. Inspired by the recently discovered mono-decker inverse sandwich D_{9h} La₂B₉⁻ (¹A'₁) (1) and based on the extensive first-principles theory calculations, we predict herein the possible existence of a series of bi-decker inverse sandwich di-lanthanide boron complexes including D_{9d} La₂[B₁₈] (³A₁₉) (**2**), D_{9d} La₂[B₁₈]²⁻ (¹A₁₉) (**3**), and C_{2h} La₂[B₂@B₁₈] (¹A₉) (**4**) which all contain a tubular B_n ligand (n = 18, 20) sandwiched by two La atoms at the two ends. In these novel clusters, La₂[B₂@B₁₈] (4) as a tubular molecular rotor with the smallest core-shell structure reported to date in boron-based nanoclusters possesses a B_2 -bar rotating constantly and almost freely inside the B_{18} tube around it at room temperature. Detailed bonding analyses indicate that these complexes are stablized by effective $(d-p)\sigma$, $(d-p)\pi$, and $(d-p)\delta$ coordination interactions between the La centers and B_n bi-decker ligand. Six multicenter fluxional σ -bonds between the B₂-core and B₁₈ tube in La₂[B₂@B₁₈] (4) are found to be responsible for its unique fluxional behaviors. The IR and Raman spectra of the concerned species are simulated to facilitate their experimental characterization.

> of the neutral at the *ab initio* theory level.¹¹ Extensive GM searches indicated that medium-sized Bn clusters favor coreshell structures,^{12,13} with B₄₆ as the smallest core-shell-like boron cluster (B_4 (a) B_{42}) predicted to date.¹⁴

> Transition-metal-doping induces dramatic structural changes and leads to earlier planar \rightarrow tubular \rightarrow spherical \rightarrow core-shell-like structural transitions in boron clusters. Transition-metal atoms with unfilled d orbitals can be comfortably coordinated at the center of 8, 9, and 10-membered boron rings, as evidenced in the experimentally observed perfect D_{8h} Co $\mathbb{O}B_8^-$, D_{9h} Ru $\mathbb{O}B_9^-$, and D_{10h} Ta $\mathbb{O}B_{10}^-$.^{15–19} CoB₁₂⁻ and RhB₁₂⁻ complexes with a B₁₂ ligand analogous to benzene were lately confirmed to have half-sandwich structures.²⁰ A family of transition-metal-centered DR tubular complexes in staggered motifs were recently confirmed in experiments, including MnB₁₆⁻, CoB₁₆⁻, RhB₁₈⁻, and TaB₂₀⁻, with TaB_{20}^{-} (B₂-[Ta@B₁₈]⁻) behaving like a tubular molecular rotor at 900 K facilitated by delocalized fluxional bonds which form and break constantly.²¹⁻²⁶ Endohedral- and exohedral-metaldoped borospherenes based on D_{2d} B₄₀ have been predicted in theory.²⁷ Various mono-metal doped small boron clusters have also been theoretically predicted.28-33 However, di-metaldoped boride clusters have been rarely investigated in both experiments and theory. $D_{6h} \operatorname{Ta_2B_6}^-$ was the first mono-decker inverse sandwich complex with a perfect B₆ ring sandwiched



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between two Ta centers.³⁴ Very recently, a series of monodecker inverse sandwich di-lanthanide boron complexes including $Ln_2B_7^-$, $Ln_2B_8^-$, and $Ln_2B_9^-$ (Ln = La and Pr) were discovered in PES measurements which all contain a perfect or an almost perfect B_n ring (n = 7, 8, and 9) sandwiched by two Ln atoms at the two ends.^{35,36} In these inverse sandwich clusters, D_{9h} La₂B₉^{- (1}A'₁) appears to be extraordinarily stable due to its $\sigma + \pi$ dual aromaticity and two fully filled $(d-p)\delta$ bonds. It is believed to be the largest mono-decker inverse sandwich complex between the lanthanide and boron due to the size effect in the B_n mono-decker ligand.³⁶ To achieve larger inverse sandwich lanthanide boride complexes, one may consider to design bi-decker or even multi-decker inverse sandwich clusters grown up from the experimentally observed stable mono-decker boron complexes in vertical directions. As mentioned above, DR tubular boron clusters with two staggered boron rings have been characterized in gas-phase experiments $(B_n^+, n = 16-25 \text{ (ref. 10)})$ or predicted in theory (like $D_{2d} B_{20}^{11}$). Such DR tubular boron clusters may serve as effective ligands to lanthanide metals to form stable bi-decker inverse sandwich complexes.

Keeping the inspiration in mind and based on extensive first-principles theory calculations, we predict herein the possibility of the bi-decker tubular inverse sandwich complexes D_{9d} La₂[B₁₈] (³A_{1g}) (2), D_{9d} La₂[B₁₈]²⁻ (¹A_{1g}) (3), and C_{2h} La₂[B₂@B₁₈] (¹A_g) (4), in which La₂[B₂@B₁₈] (4) as a tubular molecular rotor with the smallest core–shell structure reported to date in boron-based nanoclusters possesses a B₂-bar rotating constantly and almost freely inside the B₁₈ DR tube surrounding it in the radial direction at 300 K. These attractive tubular inverse sandwich complexes are effectively stabilized by (d–p) σ , (d–p) π , and (d–p) δ interactions between the two La centers and bi-decker tubular ligand and may serve as building blocks to form lanthanide boride nanomaterials with novel electronic and magnetic properties (Fig. 1).

2. Theoretical procedure

Extensive GM searches were performed on La_2B_{18} , $La_2B_{18}^{2-}$, and La_2B_{20} using the TGmin2 algorithm³⁷ at the DFT level, in conjunction with manual structural constructions based on the previously reported $B_n^{-/0/+}$ clusters (n = 18 and 20).^{10,11} More than 3000 trial structures were explored for each species in both singlet and triplet spin states at PBE/TZVP. Low-lying



Fig. 1 Optimized structures of the mono-decker inverse sandwich D_{9h} La₂(B_{9^-} (1) and bi-decker tubular inverse sandwich D_{9d} La₂(B_{18}) (2), D_{9d} La₂(B_{18})²⁻ (3), and C_{2h} La₂(B_{2} @ B_{18}) (4) at the PBE0/6-311+G(d) level, with the B–B bar at the center of La₂(B_{2} @ B_{18}) (4) highlighted in purple.

isomers were then fully optimized at the PBE038 and TPSSh39 levels with the 6-311+G* basis set⁴⁰ for B and Stuttgart relativistic small-core pseudopotential for La41,42 using the Gaussian 09 program suite,⁴³ with the vibrational frequencies checked. Single-point energies of the five lowest-lying isomers were further refined at the PBE0 geometries using the CCSD(T) method⁴⁴⁻⁴⁶ implemented in MOLPRO,⁴⁷ with the basis set of 6-311+G(d) for B and Stuttgart relativistic small-core pseudopotentials for La. TS and QST2 calculations were performed to locate the transition state (TS) of C2h La2[B2@B18] which turned out to have the same symmetry as the GM with the B_2 -center rotated about 10° inside the B_{18} tube from the GM. The intrinsic reaction coordinate (IRC)⁴⁸ calculation was carried out to confirm that the obtained structure is the true TS. Chemical bonding analyses were performed using the adaptive natural density partitioning (AdNDP) approach.49,50 Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program.⁵¹ Born–Oppenheimer molecular dynamics (BOMD) simulations were performed on La₂[B₂@B₁₈] (4) for 30 ps at 200 K, 300 K, and 400 K using the CP2K software package.52

3. Results and discussion

We start from La₂B₁₈, the smallest di-lanthanide boride cluster considered in this work. Encouragingly, extensive GM searches indicate that the GM of neutral La2B18 turns out to be the anticipated perfect bi-decker inverse sandwich D_{9d} La₂[B₁₈] $({}^{3}A_{1\sigma})$ (2) which can be constructed from the experimentally observed mono-ring inverse sandwich D_{9d} La₂[B₉]⁻ (1) by inserting one more B9 decker into the system in a staggered motif or by sandwiching a perfect D_{9d} B₁₈ DR tube with two La atoms at the two ends. Triplet $La_2[B_{18}] ({}^{3}A_{1g}) (2)$ possesses two degenerate singly occupied highest occupied molecular orbitals (SOMOs, eg), with the optimized La-La distance, La-B coordination bond length, and average B-B bond length of $r_{\text{La-La}}$ = 4.59 Å, $r_{\text{La-B}}$ = 2.78 Å, and $r_{\text{B-B}}$ = 1.67 Å, respectively. A slightly distorted singlet bi-decker inverse sandwich C_2 $La_2[B_{18}]$ appears to lie within 0.02 eV in energy relative to the GM at CCSD(T) (Fig. S1[†]). The triplet D_{9d} and singlet C_2 inverse sandwich isomers are practically iso-energetic and may coexist in experiments. Other isomers are found to lie much higher in energy (>0.56 eV) than the GM at CCSD(T). Attaching one extra electron to the triplet $La_2[B_{18}]$ (2) results in the slightly distorted degenerate bi-decker inverse sandwich Ci $La_2[B_{18}]^-$ and C_{2h} $La_2[B_{18}]^-$ due to Jahn-Teller distortions (Fig. S2[†]).

The attachment of two extra electrons to neutral La₂[B₁₈] (2) to fulfil the two degenerate SOMOs (e_g) results in the perfect singlet inverse sandwich D_{9d} La₂[B₁₈]²⁻ (¹A_{1g}) (3) with $r_{La-La} = 4.47$ Å, $r_{La-B} = 2.73$ Å, and $r_{B-B} = 1.69$ Å, respectively. As the GM of the dianion, La₂[B₁₈]²⁻ (3) lies 0.04 and 0.18 eV lower at CCSD(T) than the second (C_s) and third lowest-lying (C_{2h}) isomers which feature boron double chains, respectively (Fig. S3†). Other low-lying isomers appear to be at least 0.49 eV less stable than the GM. Detailed NBO analyses show that the

La centers in $La_2[B_{18}]^{2-}$ (3) possess the natural atomic charge of $q_{La} = +1.09 |e|$ and the electronic configuration of La[Xe] $4f^{0.16}5d^{1.75}6s^{0.07}$. Obviously, an La atom donates its 6s¹ electron almost completely to the B_{18} tubular ligand in $La_2[B_{18}]^{2-}$ (3). La- B_{18} -La coordination interactions thus mainly originate from contributions involving the La 5d² atomic orbitals. An La center in $La_2[B_{18}]^{2-}$ (3) possesses the total Wiberger bond order of $WBI_{La} = 3.23$, with each La forming nine equivalent La-B coordination interactions with the bond order of $WBI_{La-B} = 0.30$ with its neighboring B_9 decker.

Adding two more B atoms into $La_2[B_{18}]$ (2) produces La_2B_{20} , the most concerned species targeted in this work. We initially tried to construct a perfect bi-decker inverse sandwich structure for La_2B_{20} , using the previously reported DR tubular B_{20}^{11} as the ligand. However, extensive GM searches show that the B₂-centered bi-decker inverse sandwich C_{2h} La-[B₂(a)B₁₈]-La $({}^{1}A_{o})$ (4) with two staggered B₉ rings is the true GM of the neutral which lies 0.27 eV more stable than the initially designed D_{10d} La- B_{20} -La with two staggered B_{10} rings at CCSD (T). The DR tubular B_n ligands (n = 18 and 20) with two staggered B₉ rings in 2-4 dominate the high stability of these bidecker complexes. The second buckled isomer C_{s} La₂[B₂@B₁₈] which contains one B9 decker on the top and one B11 decker at the bottom in the B₂₀ ligand lies slightly higher (by 0.02 eV) than the GM. The B–B core in the GM with $r_{B-B} = 1.64$ Å possesses the average La–B distance of $r_{\text{La-B}} = 2.53$ Å which is obviously shorter than the average La-B distance of $r_{\text{La-B}}$ = 2.85 Å between La and the nine B atoms in its neighboring B₉ decker. There exists therefore a perfect La-B2-La rhombus in the GM, with B-B and La-La as the short and long axes, respectively. Interestingly, the B2-centered La-[B2@B18]-La (4) turns out to be the smallest core-shell structure in boronbased nanoclusters reported to date.¹⁴ Furthermore, extensive molecular dynamics simulations indicate that, with the small energy barrier of 2.33 kcal mol⁻¹ between the TS and GM at CCSD(T), $La_2[B_2(a)B_{18}]$ (4) behaves like a tubular molecular rotor in pseudo-rotations at 300 K, with the B₂-bar rotating constantly and almost freely inside the B₁₈ DR tube in the radial direction (Video S1[†] and Fig. 2). The transition state TS $La_2[B_2(a)B_{18}]$ with the imaginary vibrational frequency of 218i cm^{-1} appears to have the same C_{2h} symmetry as the GM $La_2[B_2 \oplus B_{18}]$ (4), with the B₂-bar at the B₁₈ DR tube center in a slightly different orientation from the GM (Table S1[†]).

La₂[B₂(a)B₁₈] (4) possesses the HOMO–LUMO gap of $\Delta E_{\text{gap}} = 2.25 \text{ eV}$ (Fig. S5†), underlying its high chemical stability. Its two equivalent La centers possess the natural atomic charge of $q_{\text{Ta}} = +1.23$ |*e*|, the electronic configuration of La [Xe]4f^{0.26}5d^{1.55}6s^{0.06}, and the total Wiberger bond order of WBI_{La} = 3.18. The average La–B coordination bond order between La and the B–B bar is calculated to be WBI_{La–B} = 0.29 which is obviously higher than the average La–B bond order of WBI_{La–B} = 0.22 between La and its neighboring B₉ decker, suggesting strong La–B coordination interactions in the La–B₂–La rhombus. Detaching one valence electron from La₂[B₂(a)B₁₈] (4) generates a stable C_{2h} La₂[B₂(a)B₁₈]⁺ monocation (Fig. S6†) which may be targeted in future experiments.



Fig. 2 Bonding fluctuations in the tubular molecular rotor $La_2[B_2@B_{18}]$ (4) at 300 K, with the rotational angle of 20° between two neighbouring GMs. The energy barrier between the GM and TS is indicated in kcal per mole at the CCSD(T) level. The fluxional 4c-2e bonds (in both GM and TS) and 3c-2e bonds (in TS) are highlighted in pink and blue, respectively.

To better interpret the high stabilities of these inverse sandwich complexes, we choose to analyze the bonding patterns of the closed-shell $La_2[B_{18}]^{2-}$ (3) and $La_2[B_2@B_{18}]$ (4) in detail using the AdNDP approach which recovers both the localized and delocalized bonds of the concerned systems. As shown in Fig. 3a, $La_2[B_{18}]^{2-}$ (3) possesses 18 equivalent 3c-2e σ bonds on 18 B₃ triangles on the B₁₈ DR tubular ligand with the occupation number of ON = 1.93 |e| in the first row. The second row contains 3 10c-2e $B_9(\sigma)$ -La($d_{\pi/\sigma}$) bonds on the top involving the top La center and its neighboring B₉ decker with ON = 1.91–1.97 |e| and 3 symmetrically distributed 10c–2e B₉(σ)–La $(d_{\pi/\sigma})$ bonds on the opposite side involving the bottom La center and its neighboring B₉ decker, forming two equivalent local $(d-p)\sigma$ aromatic systems matching the 4n + 2 rule (n = 1)in the dianion. The next 2 18c–2e σ bonds with ON = 1.99 in the third row represent the effective σ -overlap interactions between the two staggered B9 deckers in the B18 ligand. The 3 20c–2e π bonds with ON = 2.00 |e| at the end of the fourth row represent the effective $(d-p)\pi$ interactions in $La_2[B_{18}]^{2-}$ (3), resulting in a π -aromaticity in the system. The fully filled 2 20c-2e $B_{18}(\pi)$ -La₂(δ) bonds at the beginning of the fourth row also render high stability to $La_2[B_{18}]^{2-}$ (3), similar to the situation in the experimentally observed highly stable $La_2B_9^{-1}$ (1).³⁶ Overall, the bi-decker $La_2[B_{18}]^{2-}$ (3) has similar $(d-p)\sigma$, π , and δ interactions to those of the mono-decker $La_2B_9^{-}$ (1).³⁶ The 18 $3c-2e \sigma$ bonds and 2 $18c-2e \sigma$ bonds which glue the two B_9 rings together in the B_{18} bi-decker ligand in $La_2[B_{18}]^{2-}$ (3) function similar to the 9 2c-2e σ bonds in the B₉⁻ mono-decker ligand in $La_2B_9^-(1)$.³⁶

La₂[B₂(a)B₁₈] (4) inherits the main bonding characteristics of La₂[B₁₈]²⁻ (3). It has 12 3c-2e σ bonds on 12 B₃ triangles on the B₁₈ DR tube with ON = 1.91–1.95 |*e*|. The 6 B₃ triangular holes left on the B₁₈ DR tube and the B₂-bar at the center form 6 4c-2e tetragonal σ bonds with ON = 1.86–1.89 |*e*| (Fig. 2 and 3).



Fig. 3 AdNDP bonding patterns of the closed-shell (a) $La_2[B_{18}]^{2-}$ (3) and (b) $La_2[B_2@B_{18}]$ (4), with the occupation numbers (ONs) indicated.

In particular, $La_2[B_2@B_{18}]$ (4) also forms 1 4c-2e σ bonds on the La-B₂-La rhombus with ON = 1.93 |e| in the first row which mainly represents the effective B–B σ -interaction in the B_2 -bar with the bond order of $WBI_{B-B} = 0.66$. Similar to $La_2[B_{18}]^{2-}$ (3), $La_2[B_2@B_{18}]$ (4) also possesses 3 12c-2e $B_{11}(\sigma)$ - $La(d_{\pi/\sigma})$ bonds on the top and 3 symmetrically distributed 12c-2e B₁₁(σ)-La(d_{π/σ}) bonds at the bottom with ON = 1.89–1.95 |e|. These delocalized bonds each involve one La center and 11 neighboring B atoms, with the B₂-core shared by two La centers at the two ends. $La_2[B_2 \circledast B_{18}]$ (4) therefore also possesses two equivalent local $(d-p)\sigma$ aromatic systems. The 3 20c–2e σ bonds with ON = 1.99 in the third row represent the effective σ -interactions within the B₂₀ ligand. In addition, $La_2[B_2(\mathfrak{A}B_{18}]]$ (4) has 3 22c-2e π bonds at the end of the fourth row with ON = 2.00 |e|, resulting in a $(d-p)\pi$ aromatic system in the neutral. The two $(d-p)\delta$ bonds at the beginning of the fourth row are fully filled, again rendering high stability to the system. These $(d-p)\sigma$, π , and δ bonds have their origins in the canonical molecular orbitals (CMOs) of $La_2[B_2(a)B_{18}]$ (4) depicted in Fig. S5.†

The AdNDP bonding pattern of TS C_{2h} La₂[B₂@B₁₈] is presented in Fig. S7.† A close comparison indicates that the main difference between the GM and TS in bonding patterns occurs at the six delocalized σ -bonds between the B₂-bar and the neighboring boron atoms in the B₁₈ DR tube around it, with all the other σ and π bonding interactions remaining basically unchanged. In specific, the 6 4c-2e tetragonal σ bonds between the B_2 core and the B_{18} tube in C_{2h} GM (Fig. 3) have been transferred into 4 4c–2e tetragonal σ bonds between the B_2 -bar and B_{18} tube and 2 3c-2e triangular σ bonds on the B_{18} tube in the slightly less stable C_{2h} TS (Fig. S7[†]). Such a 6 4c–2e σ (GM) \rightarrow 4 4c-2e σ + 2 3c-2e σ (TS) \rightarrow 6 4c-2e σ (GM) bonding fluctuation repeats itself in the pseudo-rotation process of the tubular molecular rotor in which the B₂-bar rotates inside the B_{18} DR tube constantly at a rotational angle of 20° in each step (Fig. 2). It is these fluxional σ -bonds which form and break constantly that facilitate the unique fluxional behaviors of $La_2[B_2(a)B_{18}]$ (4) which exhibit certain similarity to that of the experimentally observed tubular molecular rotor [Ta@B₂₀]^{-.25,26} The Ta-centered [Ta@B₂₀]⁻ possesses a B₂-bar rotating constantly atop its B₁₈ DR tubular ligand at 900 K.²⁵

Joint infrared photodissociation (IR-PD) spectroscopy and first-principles investigation has proven to be an effective approach in characterizing novel clusters in the gas-phase.^{53,54} We computationally simulate the IR and Raman spectra of $La_2[B_{18}]$ (2) and $La_2[B_2@B_{18}]$ (4) in Fig. 4 to facilitate their future spectral characterization. The highly symmetrical D_{9d} $La_2[B_{18}]$ (2) possesses highly featured IR and Raman spectra, with strong asymmetrical IR active modes at 170 (a_{1u}), 751 (e_{1u}), and 859 (e_{1u}) cm⁻¹ and symmetrical Raman active vibrations at 150 (a_{1g}), 467(a_{1g}), 561 (a_{1g}), 621 (e_{1g}), and 798 (a_{1g}) cm⁻¹ represents the typical radial breathing mode (RBM) (a_{1g}) of the D_{9d} B₁₈ DR ligand which can be used to characterize tubular structures.⁵⁵

The vibrational spectra of $La_2[B_2(B_{18}]$ (4) become much more complicated due to its low geometrical symmetry, with the strong IR active modes at 346 (b_u), 603 (a_u), 716 (a_u), 786 (a_u), 928 (b_u), and 1204 (a_u) cm⁻¹ and Raman active vibrations at 235 (b_g), 526 (a_g), 599 (a_g), 703 (a_g), 785 (a_g), 991 (a_g), 1129 (a_g), and 1244 (a_g) cm⁻¹, respectively. The strongest Raman peak at 599 cm⁻¹ stands for the RBM mode (a_g) of the B₂₀ DR



Fig. 4 Simulated IR and Raman spectra of (a) $La_2[B_{18}]$ (2) and (b) $La_2[B_2@B_{18}]$ (4) at the PBE0/6-311+G(d) level.

tubular ligand, while the last Raman peak at 1244 $\rm cm^{-1}$ represents the B–B stretching vibration mode (ag) in the B2-core.

4. Conclusions

In summary, based on the recently discovered $La_2B_9^{-}(1)$ and extensive first-principles theory calculations, we have predicted a series of bi-decker inverse sandwich di-lanthanide boride clusters including D_{9d} La₂[B₁₈] (³A_{1g}) (2), D_{9d} La₂[B₁₈]²⁻ (¹A_{1g}) (3), and C_{2h} La₂[B₂@B₁₈] (¹A_g) (4). In these bi-decker complexes with two staggered B_9 rings in the ligands, $La_2[B_2@B_{18}](4)$ as a tubular molecular rotor with the smallest core-shell structure encompasses a B2-bar rotating constantly and almost freely inside the B₁₈ DR tubular unit at room temperature. The fluxionality of $La_2[B_2@B_{18}]$ (4) is facilitated by six fluxional σ -bonds between the B₂-bar and neighboring B atoms in the B₁₈ DR tube. Investigations on other di-lanthanide(Ln)-boron bi-decker inverse sandwich complexes $Ln_2[B_{18,20}]$ (Ln = Pr and Tb) and di-lanthanide-boron core-shell-like complexes $Ln_2[B_n \otimes B_m]$ with larger B_n cores $(n \ge 3)$ are currently in progress.

Conflicts of interest

There are no conflicts to declare.

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