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A highly connected metal—organic framework with a specific nonpolar nanotrap for inverse ethane/ethylene separation†

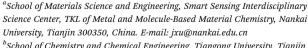
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Efficient separation of ethylene (C_2H_4) from ethane (C_2H_6) via a one-step adsorption process is desirable yet challenging. In this work, we report a C_2H_6 -selective polynuclear Tb-MOF [Tb₉(μ_3 -O)₂(μ_3 -OH)₁₂(H₂O)₉(TCPE)₃]⁻·[H₃O]⁺·(solvents)_x (TCPE = tetrakis(4-carboxyphenyl)ethylene acid), **NKU-200-Tb**, assembled via the reticular chemistry principle. The resulting (4,12)-connected framework critically features a high density of nonpolar aromatic rings on the pore surface and forms a specific nanotrap for C_2H_6 with multiple $C-H\cdots\pi$ interaction sites. As a result, **NKU-200-Tb** exhibits an inverse adsorption behavior with a high C_2H_6/C_2H_4 selectivity of 2.06 and a large uptake ratio of 151% (60.27/39.95 cm³ g⁻¹) at 298 K and 1 bar. The superior adsorption properties of **NKU-200-Tb**, combined with great structural stability, place it among the most promising stable C_2H_6 -selective MOFs. Dynamic breakthrough experiments demonstrate that polymer-grade C_2H_4 (>99.9%) can be harvested in one step from a binary mixture of C_2H_6/C_2H_4 (10/90, v/v). This work signifies the synergy of pore surface chemistry and space confinement in promoting the challenging C_2H_6/C_2H_4 separation.

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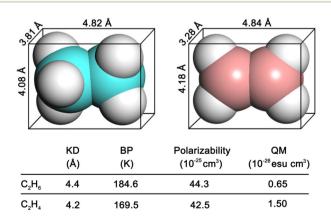
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Ethylene (C_2H_4) is one of the most important chemical feedstocks in the petrochemical industry due to its wide use in the manufacture of polymers, plastics, polyesters, and other commodity chemicals, wherein polymer-grade C_2H_4 ($\geq 99.9\%$ pure) is required.¹ However, the crude olefin products obtained through the cracking of naphtha inevitably contain a small amount of ethane (C_2H_6) impurity, and their separation is presently considered as the most challenging industrial separation ascribed to their very similar molecular dimensions and physicochemical properties (Scheme 1).² Cryogenic distillation technology is the prevalent solution in industry for separating C_2H_4 from C_2H_6 , which is usually operated in a large distillation tower (120–180 trays) at low temperatures (180–258 K) and high pressures (5–28 bar), thereby coming with a high energy penalty.³ As far as is known, purification of olefin (*i.e.*, ethylene and propylene) from paraffin (*i.e.*, ethane and propane) accounts for 0.3% of global energy use and has been regarded as one of the "seven chemical separations to change the world".⁴ Thus, developing an alternative method of purifying



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 $\label{thm:condition} \parbox{\uparrow Electronic supplementary information (ESI) available: Additional crystallographic and magnetic data. See DOI: $https://doi.org/10.1039/d3qi01595e \parbox{\downarrow} \parb$



Scheme 1 Molecular structure and physical properties of C_2H_6 and C_2H_4 , KD = kinetic diameter. BP = boiling point, QM = quadrupole moment.

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C₂H₄ in an energy-efficient manner is urgently desirable and essential to reduce energy footprint.

Adsorptive separation by porous materials has emerged as a promising technology for addressing olefin purification.^{5,6} In this regard, metal-organic frameworks (MOFs) have great advantages over conventional porous solids (e.g., zeolites, activated carbon, and mesoporous silica) in terms of gas adsorption selectivity and capacity, on account of their programmable pore structures and customizable pore environments.^{7,8} Over the past decade, many MOF adsorbents have been designedly constructed and shown preferential adsorption of C2H4 over C_2H_6 , relying on molecular sieving, 9,10 π -complexation, 11 or electrostatic interaction between the π -clouds of olefin and highly polar groups (e.g., open metal sites).12 In order to obtain polymer-grade ethylene, these C2H4-selective adsorbents have to be subjected to multiple adsorption-desorption cycles to remove the co-adsorbed impurity, inevitably involving energy-intensive desorption and regeneration steps by temperature or vacuum swing.¹³ In contrast, the adsorbents with inverse adsorption selectivity for C2H6 over C2H4 can harvest pure C₂H₄ directly at the outlet through a single-step adsorption process with about 40% energy saving. 14-17 However, such C2H6-selective adsorbents reported to date are much fewer than the C₂H₄-selective ones probably due to two major reasons: first, the kinetically driven separation or molecular sieving is inaccessible for achieving inverse adsorption behavior in rigid MOFs, as the kinetic diameter of C₂H₆ is larger than that of C₂H₄. Second, there is a lack of suitable strong paraffin affinity sites compared with olefin, bringing difficulty in designing delicate pore environments to trap C_2H_6 .

In recent five years, significant efforts have been dedicated to the construction of non-trivial paraffin-selective MOFs and gained much progress. 18 Among the proposed design strategies, the most sophisticated one is to customize an inert/ hydrophobic pore surface composed of nonpolar aromatic rings or aliphatic chains in the absence of open metal sites, which is envisaged to attain more nonspecific van de Waals (vdW) interactions with C₂H₆ due to its larger polarizability than C_2H_4 (44.3 × 10⁻²⁵ cm³ vs. 42.5 × 10⁻²⁵ cm³) and more C-H binding sites.¹⁹ With this principle, a series of C₂H₆-selective MOFs have been successfully fabricated, 20-23 but many of them suffer from insufficient C₂H₆/C₂H₄ selectivity (<2) partly due to the relatively weak interaction nature of vdW forces. One straightforward way to overcome this dilemma is increasing the number of such vdW interactions by promoting the density of functional affinity sites or enhancing confinement to enlarge the contact area of the pore surface with gas molecules, both of which are, however, still underexplored. In addition to adsorption properties, the structural stability of adsorbents should also be considered. For example, Fe₂(O₂) (dobdc) with a record C₂H₆/C₂H₄ selectivity has to be operated in a glove box because of its poor stability in environments, 15 greatly hindering its industrial application.

Bearing these in mind, we sought to explore the adsorption and separation performance of a (4,12)-connected Tb-MOF, namely NKU-200-Tb, 24 based on a nonanuclear Tb9 node and

the aromatic linker tetrakis(4-carboxyphenyl)ethylene acid (H₄TCPE, Fig. S1 and S2†), due to the following considerations. First, its highly connected shp network constitutes a large π -conjugated system enriched with nonpolar aromatic rings, promoting the density of functional affinity sites for C2H6. Second, its framework contains three types of channels with different shapes and apertures, holding high promise to offer suitable confinement and multi-site adsorption for C₂H₆. Third, the high connectivity of the framework and the strong coordination bond between the Tb3+ ion (hard Lewis acid) and carboxylate ligand (hard Lewis base) endow it with excellent structural stability. In line with the above analyses, NKU-200-**Tb** shows the desired inverse adsorption behavior with a high C₂H₆/C₂H₄ selectivity of 2.06 at 298 K and 1 bar, surpassing many reported C2H6-selective MOFs. Further density functional theory (DFT) calculations disclose that the aperture window of one channel with suitable pore size forms a nanotrap to promote the C₂H₆/C₂H₄ separation by the enhanced confinement. As a result, NKU-200-Tb achieves a good performance for purifying C₂H₄ (>99.9%) in one step from a binary mixture of C₂H₆/C₂H₄ (10/90, v/v), as demonstrated by breakthrough experiments, placing it among the promising one-step C₂H₄ purification adsorbents.

The crystalline NKU-200-Tb was synthesized according to our previous report.²⁴ Single-crystal X-ray diffraction analysis reveals that it crystallizes in the trigonal space group $P\bar{3}$ with the formula $[Tb_9(\mu_3-O)_2(\mu_3-OH)_{12}(H_2O)_9(TCPE)_3]^- \cdot [H_3O]^+ \cdot (solvents)_x$ (Fig. S3 and Table S1†). In this structure, the nonanuclear carboxylate-based cluster $[Tb_9(\mu_3-O)_2(\mu_3-OH)_{12}(H_2O)_9(O_2C-)_{12}]^-$ is formed and it has a two-fold disorder with equal occupancy (Fig. S4†). In each Tb₉ cluster, nine Tb³⁺ ions are arranged in a tricapped trigonal prism (Fig. S5†): six Tb³⁺ ions are 8-coordinated with two carboxylate groups from individual TCPE4ligands, four μ_3 -OH, one μ_3 -O, and one terminal water ligand in a distorted bicapped trigonal prismatic geometry (Fig. S6a†), while the other three coordinate to four carboxylates of four $TCPE^{4-}$ ligands, four μ_3 -OH, and one apical water molecule, showing a distorted tricapped trigonal prism geometry (Fig. S6b†). From a topological viewpoint, the hexagonal prismatic Tb₉ cluster (Fig. 1b) and the rectangular TCPE⁴⁻ ligand (Fig. 1a) serve as a 12-connected (12-c) and 4-c node to yield a (4,12)-c shp net (Fig. 1d). The resulting highly connected framework features a high density of aromatic rings from TCPE⁴⁻, constituting a large π-conjugated pore surface and encompassing three types of one-dimensional (1D) channels. Among them, the largest channel A has a triangular aperture with an equilateral side length of 9.5 Å running along the c-axis (Fig. 1c), while the rhombus channel B and the isosceles triangular channel C are elongated along both the a- and b-axis, with the pore diameters of 7.0 and 4.5 Å, respectively (Fig. 1e and f). The total guest-accessible volume calculated using PLATON is 35.3% of the unit-cell volume, affording enough space for gas accommodation.

The phase purity of the as-synthesized sample was verified by comparing the experimental powder X-ray diffraction (PXRD) pattern to the simulation result. Immersing the

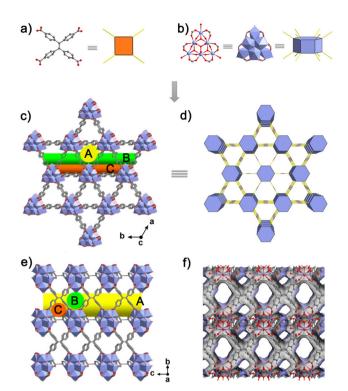


Fig. 1 (a and b) The 4-c TCPE⁴⁻ ligand and the 12-c nonanuclear Tb₉ cluster. (c and e) The 3D framework of NKU-200-Tb with three types of 1D channels along the c- and a-axis, respectively. (d) The topological simplification of the (4,12)-c shp net. (f) View of channels B and C in the Connolly surface.

sample in a series of organic solvents and aqueous solutions with a broad pH range of 3-12 for 24 h gave no indication of decomposition or crystallinity loss in PXRD profiles (Fig. S7 suggesting its great chemical stability. Thermogravimetric (TG) analysis further reveals that the framework does not decompose until 500 °C (Fig. S9†), also supported by the variable-temperature (VT) PXRD data (Fig. S10†). Thus, the excellent structural stability of NKU-200-**Tb** under harsh thermal and chemical conditions places it among the most stable C₂H₆-selective MOFs reported in the literature (Table S2†), which should be attributed to not only the high connectivity of the framework, but also the strong coordination bond between the Tb3+ ion and carboxylate oxygen atom, according to the concept of hard and soft acids and bases (HSAB).²⁵ In order to investigate the permanent porosity of NKU-200-Tb, the sample was then subjected to methanol exchange and dynamic vacuum activation at 150 °C for 12 h. The unchanged PXRD curve confirms again the retention of its structural integrity and crystallinity after desolvation (Fig. S7†). The N₂ adsorption-desorption experiment on NKU-200-Tb at 77 K shows a reversible type-I isotherm (Fig. S11†), indicative of its microporous characteristic. The corresponding Brunauer-Emmett-Teller (BET) surface area and the total pore volume are then determined to be 792.7 m² g⁻¹ and 0.32 cm³ g^{-1} (calculated by a single point method at $P/P_0 = 0.90$), respectively, very close to the theoretical pore volume value of

0.35 cm³ g⁻¹ derived from single-crystal structural analysis. The estimated pore size distribution using nonlocal density functional theory lies in the range of 7-10 Å (Fig. S11†), also in agreement with the crystallographic data. The high structural stability and porosity of NKU-200-Tb, also proved by the N2 adsorption curves after harsh treatments (Fig. S12†), pave the way for gas adsorptive separation.

The single-component adsorption isotherms of NKU-200-Tb for C₂H₆ and C₂H₄ were measured at 273 and 298 K, respectively. As shown in Fig. 2a and b, this Tb-MOF exhibits the desirable adsorption preference for C_2H_6 over C_2H_4 at both temperatures and throughout the whole pressure region, fulfilling the demand for one-step C₂H₄ purification from binary C₂H₆/C₂H₄ mixtures. At 298 K and 1 bar, the adsorption uptake of C_2H_6 on **NKU-200-Tb** reaches up to 60.27 cm³ g⁻¹ (2.69 mmol g^{-1}), much higher than that of C_2H_4 (39.95 cm³ g⁻¹, 1.78 mmol g⁻¹) with a large uptake ratio of 151%, surpassing many leading C2H6-selective MOFs (Table S3†). We envisioned that the adsorption affinity order of C₂H₆ > C₂H₄ on NKU-200-Tb is a consequence of its nonpolar/hydrophobic pore surface. To validate the pore surface polarity, we also collected the CO₂ and water vapor adsorption isotherms at 298 K. As seen from Fig. S13,† the CO₂ uptake increases slowly and constantly over the whole pressure range and reaches $32.99 \text{ cm}^3 \text{ g}^{-1}$ (1.47 mmol g⁻¹) at 1 bar, much lower than that

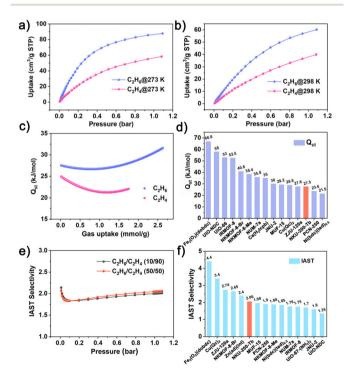


Fig. 2 (a and b) The adsorption isotherms for C_2H_6 and C_2H_4 on NKU-200-Tb at 273 and 298 K, respectively. (c) The coverage-dependent Q_{st} curves of C_2H_6 and C_2H_4 . (d) Comparison of the zero-coverage $Q_{\rm st}$ of C_2H_6 with those of some representative C_2H_6 -selective MOFs. (e) IAST selectivities for C₂H₆/C₂H₄ (50/50 and 10/90, v/v) mixtures at 298 K and 1 bar. (f) Comparison of the C₂H₆/C₂H₄ (50/50, v/v) selectivity at 298 K and 1 bar with those of top-performing C₂H₆-selective MOFs.

of C₂H₆, excluding the presence of open metal sites that have high affinity for CO₂. ^{26,27} As for water vapor, the adsorptiondesorption isotherm displays a typical S-shaped curve with a hysteresis loop and an inflection point at a relatively high moisture level (Fig. S14†). This result indicates a low binding affinity toward H₂O and manifests the hydrophobicity of the inner pore surface of NKU-200-Tb, 16,28,29 in line with the presence of abundant aromatic rings in this system.

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To quantitatively assess the binding affinities of NKU-200-**Tb** toward C_2H_6 and C_2H_4 , we calculated the isosteric enthalpy of adsorption (Q_{st}) using the virial equation based on the isotherms at 273 and 298 K (Fig. S15, S16 and Table S4†). The estimated zero-coverage Q_{st} for C₂H₆ is 27.54 kJ mol⁻¹, higher than the value of 24.93 kJ mol⁻¹ for C₂H₄ (Fig. 2c), thus reflecting a binding affinity order of C₂H₆ > C₂H₄ on NKU-200-Tb consistent with the inverse adsorption isotherms (Fig. 2a and b). Besides that, the coverage-dependent $Q_{\rm st}$ curve of C_2H_6 displays an overall ascending trend, indicative of favorable adsorbate-adsorbate interactions at higher loadings, 30,31 whereas that of C₂H₄ shows an apparent descending trend in the initial coverage range. Such an enlarged discrepancy in Qst values also benefits the challenging C₂H₆/C₂H₄ separation. Noteworthily, the zero-coverage Q_{st} of C_2H_6 on NKU-200-Tb is significantly lower than those of many benchmark C₂H₆-selective MOFs (Fig. 2d), including NKMOF-Br/-Me (40.8/38.4 kJ mol^{-1}), ¹⁴ $\text{Fe}_2\text{O}_2(\text{dobdc})$ (66.8 kJ mol^{-1}), ¹⁵ IR-MOF-8 (52.5 kJ) mol⁻¹), ²⁰ and UiO-66 (53 kJ mol⁻¹). ³² The comparatively low $Q_{\rm st}$ value will facilitate the regeneration of NKU-200-Tb by avoiding harsh treatments and high energy consumption.

In order to evaluate the separation ability of NKU-200-Tb, we employed the ideal adsorbed solution theory (IAST) to estimate the adsorption selectivities for C₂H₆/C₂H₄ mixtures with different composition ratios. By fitting the isotherms according to the dual-site Langmuir-Freundlich equation (Fig. S17 and S18†), the C_2H_6/C_2H_4 (50/50 and 10/90, v/v) selectivities are calculated to be 2.06 and 2.01, respectively, at 298 K and 1 bar (Fig. 2e). It is worth noting that the C_2H_6/C_2H_4 (50/50, v/v) selectivity on NKU-200-Tb (2.06) is superior or comparable to those of most top-performing C2H6-selective adsorbents (Fig. 2f and Table S3†), such as PCN-250 (1.9),³³ JNU-2 (1.6),³⁴ Ni(bdc)(ted)_{0.5} (1.85),³⁵ UiO-67-(NH₂)₂ (1.7),³⁶ and Zn(ad)(int) (2.4),37 and only significantly lower than those of NKMOF-Br (2.65), ¹⁴ Fe₂(O₂)(dobdc) (4.4), ¹⁵ ZJU-120a (2.74), ²¹ and Cu(Qc)₂ $(3.4)^{22}$

Such a high C₂H₆/C₂H₄ selectivity on NKU-200-Tb inspired us to further explore its actual separation performance. Fixedbed dynamic breakthrough experiments were then performed at 298 K and 1 bar, with a total inlet flow rate of 10.0 mL min⁻¹ by using He as the carrier gas (50%, vol%). When a C₂H₆/C₂H₄ gas mixture of an industrially relevant composition (10/90, v/v) was passed through the packed column of activated NKU-200-Tb, C₂H₄ was first eluted from the outlet at 314 s and quickly reached saturation, whereas the C2H6 impurity was still retained in the column for an additional time of 104 s, during which the C₂H₄ gas with high purity (>99.9%) can be directly harvested (Fig. 3a). The breakthrough experiments

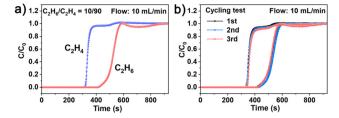


Fig. 3 (a) Dynamic breakthrough curves for a binary C₂H₆/C₂H₄ (10/90, v/v) mixture. (b) Cyclic breakthrough tests under the same conditions. All the breakthrough experiments were performed at 298 K and 1 bar, with a total flow rate of 10 mL min⁻¹ using He as the carrier gas (50%,

prove that NKU-200-Tb is capable of separating pure C2H4 from a low-level of C2H6 through one-step adsorption without resorting to energy-intensive desorption steps. We also conducted the breakthrough experiments for an equimolar C2H6/ C₂H₄ mixture and the results demonstrate that this MOF can also achieve one-step C2H4 purification from mixtures with high concentrations of C₂H₆ (Fig. S19†). For industrial applications, the stability and recyclability of an adsorbent are also important. Cyclic breakthrough tests confirm that its separation performance could be well preserved for three continuous cycles without noticeable deterioration in retention time (Fig. 3b), wherein the adsorbent was easily regenerated by heating at 150 °C under He flow for 5 h after each cycle.

To gain insight into the preferential adsorption of C₂H₆ over C₂H₄ on **NKU-200-Tb** at the molecular level, we performed DFT calculations to unveil the preferred adsorption sites and gas-framework interactions. The optimization results reveal that the most favorable trapping site for both C2H6 and C2H4 is situated at the rhombus aperture window of channel B (i.e., on the pore wall of channel A) encompassed by two Tb₉ clusters and two TCPE⁴⁻ ligands (Fig. 1e), which can be conceived of as a nanotrap (7.0 Å) possessing dense aromatic rings and suitable size for C₂H₆/C₂H₄ separation.³⁸ Within this confined space, the two C2 hydrocarbon molecules adopt distinct positions and orientations (Fig. 4). With a larger vdW surface area and more C-H binding sites, C₂H₆ is grasped at the nanotrap center with an orientation perpendicular to channel B. In contrast, C₂H₄ is located close to only one side of the aperture and oriented parallel to the a-/b-axis in channel B. As a result, one C_2H_6 molecule forms seven $C-H\cdots\pi$ (3.099–3.873 Å) interactions with all four neighboring phenyl rings from two TCPE⁴⁻ ligands, giving a static binding energy of -47.7 kJ mol⁻¹ (Fig. 4a), while one C₂H₄ molecule is in contact with only one phenyl ring via one C-H $\cdots\pi$ (3.192 Å) bond with a lower binding energy of -36.3 kJ mol⁻¹ (Fig. 4b). Clearly, the differences in the number and distance of C-H \cdots π interactions account for the preferential adsorption of C2H6 over C2H4 and the discrepancy between the static binding energies also explains the binding affinity order of $C_2H_6 > C_2H_4$ manifested in the $Q_{\rm st}$. The calculation results not only show the effectiveness of promoting the density of aromatic rings to enhance

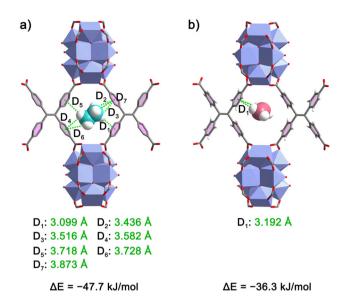


Fig. 4 (a and b) Predicted adsorption sites, interactions, and binding energies (ΔE) of C₂H₆ and C₂H₄ in the nanotrap of NKU-200-Tb obtained from the DFT optimization. The green dashed lines refer to C- $H \cdots \pi$ interactions

C₂H₆ trapping and recognition ability, but also signify the synergy with pore space confinement.

In summary, a highly connected Tb-MOF (NKU-200-Tb) was employed to implement one-step C₂H₄ purification. Based on the reticular assembly of a nonanuclear Tb9 cluster and the aromatic ligand TCPE⁴⁻, the resulting MOF not only exhibits great thermal and chemical stability, but also possesses an inert/hydrophobic pore surface composed of dense nonpolar aromatic rings. As a result, NKU-200-Tb shows a higher adsorption capacity for C₂H₆ (60.27 cm³ g⁻¹) than for C₂H₄ (39.95 cm³ g⁻¹) at 298 K and 1 bar, highlighted with an uptake ratio of up to 151% and an excellent inverse C2H6/C2H4 selectivity of 2.06, surpassing many leading C2H6-selective MOFs. Further DFT calculations disclose that two Tb9 clusters and two TCPE⁴⁻ ligands constitute a specific size-matching nanotrap to promote the C2H6 adsorption by providing abundant $C-H\cdots\pi$ interactions within a confined pore space. With the above advantages, this MOF realizes the desirable one-step acquisition of polymer-grade C₂H₄ (>99.9%) from a binary C₂H₆/C₂H₄ (10/90, v/v) gas mixture with good recyclability, as demonstrated by breakthrough experiments. Our work not only reports a new example of one-step C2H4 purification adsorbents, but importantly also sheds new light on the design of paraffin-selective MOFs in terms of the engineering of inert/nonpolar pore surfaces with an enhanced confinement effect.

Author contributions

Jing-Jing Pang: investigation, visualization, data curation, and writing - original draft. Zhi-Han Ma, Qiang-Qiang Yang, Kuo

Zhang, and Xin Lian: data curation. Hongliang Huang and Zhao-Quan Yao: formal analysis, conceptualization, and supervision. Baiyan Li: validation. Jian Xu: supervision, conceptualization, writing - review & editing, and funding acquisition. Xian-He Bu: resources.

Conflicts of interest

There are no conflicts to declare.

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