Low-Dimensional Materials



Extrinsic Green Photoluminescence from the Edges of 2D Cesium Lead Halides

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Since the first report of the green emission of 2D all-inorganic CsPb₂Br₅, its bandgap and photoluminescence (PL) origin have generated intense debate and remained controversial. After the discovery that PL centers occupy only specific morphological structures in CsPb₂Br₅, a two-step highly sensitive and noninvasive optical technique is employed to resolve the controversy. Same-spot Raman-PL as a static property-structure probe reveals that CsPbBr₃ nanocrystals are contributing to the green emission of CsPb₂Br₅; pressure-dependent Raman-PL with a diamond anvil cell as a dynamic probe further rules out point defects such as Br vacancies as an alternative mechanism. Optical absorption under hydrostatic pressure shows that the bandgap of CsPb₂Br₅ is 0.3–0.4 eV higher than previously reported values and remains nearly constant with pressure up to 2 GPa in good agreement with fullfledged density functional theory (DFT) calculations. Using ion exchange of Br with Cl and I, it is further proved that $CsPbBr_{3-x}X_x$ (X = Cl or I) is responsible for the strong visible PL in $CsPb_2Br_{5-x}X_x$. This experimental approach is applicable to all PL-active materials to distinguish intrinsic defects from extrinsic nanocrystals, and the findings pave the way for new design and development of highly efficient optoelectronic devices based on all-inorganic lead halides.

2D organic-inorganic lead halides have emerged as new hybrid perovskites with higher environmental stability and bandgap tunability than their 3D counterparts.^[1-7] Recent discovery of edge states in Ruddlesden-Popper (R-P) perovskites make them more suitable for solar cells owing to accelerated exciton dissociation rate and enhanced carrier life time in edge states although their nature and underlying mechanism remain unclear.[8-10] Because of the higher stability of all inorganic perovskites compared to that of hybrid perovskites, 3D cesium lead halides has also attracted considerable attention, especially after the observation of nearly 100% photoluminescence quantum yield of CsPbBr3 nanocrystals.[11-16] CsPb2Br5, a water-stable 2D lead halide with Cs as a spacing layer between edge-sharing PbBr₆ octahedrons, was synthesized long ago,^[17,18] but only after the first report of highly luminescent CsPb₂Br₅

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nanoplatelets and its other halides through ion exchange with Cl and I did they become widely investigated for optoelectronic properties and device applications.^[19] Strong green photoluminescence (PL), high efficiency light emitting diodes (LEDs), photodetectors, and even lasers have been repeated or demonstrated.^[17,20–27]

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In the midst of extensive studies of CsPb₂Br₅, however, a serious discrepancy emerged. CsPb₂Br₅ synthesized by several groups, in nanometer size or as large as millimeter, is transparent and exhibits no green PL.^[28–31] Density functional theory (DFT) calculations also confirm that CsPb₂Br₅ is an indirect semiconductor with a wide bandgap of $\approx 3.0 \text{ eV}$.^[28,30–32] On the other hand, some researchers initially synthesized transparent large crystals of CsPb₂Br₅ and believed it as a PL-inactive wide bandgap semiconductors,^[31] but later they changed their mind after the synthesis of highly luminescent crystals and considered defects such as Br vacancies as the sources for the bright PL.^[17] Some papers also send very confusing or conflicting messages about the source of the PL. For example, they claim CsPb₂Br₅ as PL-inactive, but either their data clearly show green PL,^[30,32] or they acknowledged a possible PL contribution from defect states.^[33] Many groups were aware of this controversy but showed no attempt to resolve the issue.^[34–37]

The root causes for these controversies and debates, i.e., the actual bandgap, and whether green emission comes from embedded CsPbBr3 nanocrystals or point defects such as Br vacancies in CsPb₂Br₅, are the lack of sensitive detection method and one-to-one relationship between the property (PL) and structure, as well as the lack of a suitable technique to distinguish different luminescent centers.^[38] In other words, the experimental evidences from opposite sides are not strong enough. For example, the observation of CsPbBr3 nanocrystals in CsPb₂Br₅, by either X-ray diffraction (XRD) or transmission electron microscopy (TEM), proves that CsPbBr₃ nanocrystals may be a possible source for the green emission, but it cannot exclude the possibility of defect contribution.^[28,33,39] Conversely, the conclusion of luminescent CsPb2Br5 based on TEM observation of pure CsPb2Br5 is problematic because PL on the same TEM spot was typically not confirmed or reported.^[17,20,24,40,41] It is well known that XRD is not a technique sensitive enough for detection of minority phases; while TEM is a local probe, it has to be combined with the same spot PL to connect structure to property.^[38,42] In order to resolve this controversy, we employ two highly sensitive and closely related methods that can

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directly correlate PL with the structure, and then distinguish point defects from embedded nanocrystals as luminescent centers. We also point out that CsPb₂Br₅ has a bandgap higher than previously reported, and discovered unique responses of its band structure and lattice vibrations to hydrostatic pressures due to its 2D layered material.

Large-size PL-inactive CsPb2Br5 sheets and highly luminescent CsPb₂Br₅ nanoplatelets were synthesized according to the reported methods.^[19,30] CsPbBr₃ micropowders and highly luminescent CsPbBr3 nanocrystals were synthesized as reference samples for PL and Raman spectroscopy.^[12,13,43] We also used CsPbBr₃ micropowders to synthesize CsPb₂Br₅ by dropping CsPbBr₃ micropowders in water or by pouring water on them. As shown in Figure S1 (Supporting Information), the change of color from orange to white indicates a quick transformation from CsPbBr3 to CsPb2Br5 Similar to previous report, the CsPb₂Br₅ white powders emit much brighter green fluorescence than the original CsPbBr3 micropowders under UV LED light.^[17] A closer look under an optical microscope in Figure 1a-c, however, reveals that the surfaces of CsPb₂Br₅ white powder grains appears dark, while their edges are bright, which is very different from CsPbBr₃, where the whole body emits green light quite uniformly. Smaller CsPb₂Br₅ platelets synthesized using the method in ref. ^[19] also display similar edge emission as long as they can be optically resolved (Figure 1d). These edge emissions are reminiscent of those observed in R-P 2D perovskites,^[8-10] but have not been reported or clarified in luminescent CsPb₂Br₅ platelets.

To confirm and understand the edge emission, we collected square-shaped CsPb₂Br₅ microplatelets from the surface of CsPb₂Br₅ synthesis water solution.^[18] Two types of platelets were observed. The first type showed no photoluminescence at all. Figure 1e-f shows optical and scanning electron microscopy (SEM) images of such "dark" platelet: both edges and top surface are extremely smooth. Figure 1g shows the other type of platelet where some locations of edges are bright but the body of the platelet is dark under laser excitation. Figure 1h reveals that bright edges are decorated with individual nanobumps while dark edges are smooth without any bumps as in Figure 1f. These new observations lead us to conclude that single crystal CsPb₂Br₅ is a wide bandgap semiconductor and transparent to visible light; bright edge emissions come from nanobumps on the edges. Figure 1i-l shows SEM, confocal PL mapping, and PL spectra of a luminescent CsPb₂Br₅ platelet. The good overlap between PL mapping and SEM image confirms these bumps as the source for the edge emission.

Edges are inevitable terminations of 2D crystals, and are typically sources for defects that can greatly degrade device performance. To identify the underlying structure that is responsible for the bright green photoluminescence, we chose a closely related optical technique, Raman scattering, to accomplish this challenging task. Compared with XRD and TEM, Raman is a more sensitive but noninvasive technique. More importantly, Raman spectroscopy has the same probing volume as PL such that property (PL) and structure (Raman) can be correlated one to one on the same spot and at same length scale. As a first step, we performed a Raman mapping on the top left corner of the plate in Figure 1i–l where PL is the strongest.^[44] The Raman mapping in **Figure 2**a,b reveals two distinct regions: a







Figure 1. Optical, photoluminescence and scanning electron microscopy images of CsPbBr₃ and CsPb₂Br₅ as well as their PL spectra. PL images of a) CsPb₂Br₃, b,c) CsPb₂Br₅ microplates, and d) CsPb₂Br₅ nanoplates under 365 nm UV illumination. e,f) Optical and SEM images of a nonemissive CsPb₂Br₅ platelet. g,h) PL and SEM images of an edge-emitting CsPb₂Br₅ platelet. PL was excited by a 473 nm laser. i–l) SEM, scanning confocal microscopy intensity mapping and PL spectrum of another edge-emitting CsPb₂Br₅ platelet. PL was excited by a 488 nm laser.

green region from the edge defined by a complete (depolarized) Raman spectrum (green) and red inner region characterized by two phonon peaks with B_{2g} symmetry. The strongly polarized B_{2g}-spectra in the inner region indicate a good single crystal quality of the CsPb₂Br₅ platelet.^[44] Conversely, the emergence of all active modes indicates the presence of multiple CsPb₂Br₅ domains with different crystal orientations, i.e., polycrystalline CsPb₂Br₅. The lack of CsPbBr₃ Raman on the edge is due to dominant CsPb₂Br₅ Raman and weak broad feature of CsPbBr₃ at lower wavenumbers at room temperature. To overcome this problem, we then used a single grating high throughput spectrometer and chose the two-phonon line of CsPbBr₃ at 310 cm⁻¹ where there is no Raman feature CsPb2Br5. Figure 2c clearly shows the two-phonon line of CsPbBr3 on the top of broad PL background from the big bump excited by a 532 nm laser, indicating that CsPbBr₃ is mixed with CsPb₂Br₅ in the bump and is contributing to the green PL emission.^[44-46]

Having obtained Raman signatures of both $CsPbBr_3$ and $CsPb_2Br_5$ from luminescent edge of large $CsPb_2Br_5$ platelets, we chose 473 nm laser to excite PL and 632.8 nm laser to detect Raman so that Raman and PL spectra can be well separated. We applied this combined Raman-PL to the $CsPb_2Br_5$ nanoplatelets by focusing two laser beams on the same spot. Figure 2d

shows Raman of the nanoplatelet ensemble: the spectrum is dominated by two of the Raman lines of $CsPb_2Br_5$ at B_{1g}/A_{1g} mode at 81 cm⁻¹ and A_{1g} at 133 cm⁻¹, but the 310 cm⁻¹ line of $CsPbBr_3$ is still well visible. We further pushed the technique to the single platelet. Figure 2e–g shows the simultaneous observation of green PL and $CsPbBr_3$ Raman spectra despite very weak Raman signal. Note that unlike large $CsPb_2Br_5$ plates, Figure 2h,i shows that the top surface of small platelets is decorated with smaller nanoplatelets besides structures on the edge.

The coexistence of both CsPbBr₃ and CsPb₂Br₅ on the edge can be directly verified by TEM. **Figure 3**a shows lattice images of a bump near the surface observed with atomic-resolution low dose aberration-corrected TEM.^[47,48] Lattice images and their electron diffraction patterns indicate that the region I is CsPbBr₃, but region II exhibits a distorted lattice and can only be indexed as a mixture of CsPbBr₃ and CsPb₂Br₅. Because the platelet is single crystal CsPb₂Br₅, this TEM reveals a gradual phase transition from CsPbBr₃ edges to the CsPb₂Br₅ single crystal. To obtain a clear picture of this phase transition, we chose another platelet and used a focused ion beam (FIB) to carve out a cross-section. Figure 3b shows a top down SEM image of the platelet, its crosssection SEM and PL spectrum are shown in Figure 3c,d. Energydispersive X-ray spectroscopy (EDS) mapping in Figure 3e,f



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Figure 2. Identification of green emission with SEM and combined Raman-PL. a,b) Three Raman modes used for the confocal Raman mapping of top left corner of the platelet shown in Figure 1i. c) Raman spectrum of the big bump in (b) excited by a 532 nm laser. d) Raman spectrum of an ensemble of $CsPb_2Br_5$ nanoplates shown in Figure 1d. Inset shows the zoom-in view of Raman near 310 cm⁻¹. e,f) Room temperature PL of an individual $CsPb_2Br_5$ nanoplate. e) Four PL images of the platelet at four edge locations excited by a 473 nm laser. Representative f) PL and g) Raman spectra of the nanoplatelet in (e). h,i) Typical SEM images of nanoplatelets similar to those in Figure 1d and panel (e) of this figure.

clearly indicates a gradual phase transition from $CsPbBr_3$ to $CsPb_2Br_5$ and a sharp interface between the single crystal region of the platelet and bump on the edge.

Having established one-to-one correlation between green PL and Raman of CsPbBr₃, and identified the contribution of CsPbBr₃ to the green PL, the next question is how to rule out the alternative mechanism, i.e., defects such as Br vacancies. The combined Raman-PL can be used to quantify CsPbBr₃ in principle, because Raman is excited below the PL transition energy, it is nonresonant and not sensitive to the quality of material in terms of native defects. The PL quantum yield, however is very sensitive to the size and quality of a material. It is well known that CsPbBr₃ nanocrystals can have near-unit PL quantum yield, but micropowders of CsPbBr₃ has PL quantum yield as low as 0.1%, which is the reason why CsPbBr₃

micropowders show very weak PL under UV LED.^[16,49] Note that the current Raman-PL at room temperature and ambient pressure is an environmental static probe. A dynamic probe allows to investigate material response to external stimulus that can help in distinguishing different luminescent centers.^[38] We chose hydrostatic pressure as an external stimulus generated by a diamond anvil cell (DAC) because DAC is compatible with optical characterizations.^[50,51] As a first step, we investigate the effect of pressure on the bandgap of CsPb₂Br₅. **Figure 4**a,b shows the pressure dependent absorption spectrum of a large size, transparent, PL-inactive CsPb₂Br₅ sheet. There is very little change in the absorption spectrum and bandgap until the pressure increases above 2 GPa.

The DFT calculations of electronic band structure and Raman active phonon evolution with pressure in CsPb₂Br₅







Figure 3. Transmission electron microscopy, PL, and energy-dispersive X-ray spectroscopy investigations of green emitting bumps in $C_SPb_2Br_5$ platelets. a) TEM phase image of the tip of a bump. Close-up and filtered sections of the phase images as indicated by regions I and II; FFT electron diffraction patterns of the lattice in I and II. b) Top-down SEM image of another $C_SPb_2Br_5$ platelet before focused ion beam milling. c) Cross-sectional SEM image of an FIB-milled slice indicated by the yellow bar in (b). Two arrows indicate the same bump before and after FIB. d,e) PL, SEM, and EDS mapping of the bump. f) Cs, Pb, and Br atomic fractions along the line indicated in (e).

reproduce very well the experimental observations in Figure 4. The DFT band structure calculations^[52] were done using Heyd–Scuseria–Ernzerhof (HSE) hybrid functional^[53] and taking into account the spin–orbit coupling (SOC). The phonon calculations were performed at a local density level of theory. The calculation details are given in the Supporting Information. **Figure 5**a presents the electronic band structure of CsPb₂Br₅ calculated at 0 and 2 GPa hydrostatic pressure. The calculated energy bandgap E_g is 3.45 eV and it is consistent with the experimental absorption edge shown in Figure 4b,c. The changes of the band structure with pressure up to 2 GPa are remarkably small in accordance with the experimental results in Figure 4c.

To get a better insight of band structure modification with lattice strain, we did a series of DFT calculations of $CsPb_2Br_5$ at different axial, tensile and biaxial compressive stresses.

The resulting changes of the bandgap, $\Delta E_{\rm gr}$, with Pb–Br bond lengths are presented in Figure 5b along with those at 2 GPa (red star). Given the range of bandgap changes with bond strains, it is evident that the Pb–Br bond length change at 2 GPa produces very little modification in the band structure. One of the reasons for the observed electronic band structure response to hydrostatic pressure is the lack of 3D Pb–Br framework in CsPb₂Br₅. At moderate isotropic pressure the chemical bonds in CsPb₂Br₅ tend more to bend, i.e., changing angles α and β (inset in Figure 5b) rather than varying bond lengths.

In Figure 4d, the Raman phonon lines with symmetry A_{1g} (51 cm⁻¹), B_{2g} (69 cm⁻¹), B_{1g} (80 cm⁻¹)/ A_{1g} (81 cm⁻¹), and A_{1g} (133 cm⁻¹) can be resolved^[44] and their evolution with hydrostatic pressure traced as shown in Figure 4e. B_{2g} (69 cm⁻¹) and A_{1g} (133 cm⁻¹) phonons are of particular interest because







Figure 4. Pressure-dependent optical absorption and Raman of $C_{S}Pb_{2}Br_{5}$. a) Absorption spectra of a transparent PL-inactive $C_{S}Pb_{2}Br_{5}$ sheet. b) Zoomed-in view of the spectra below ≈ 2 GPa. c) Pressure-dependent bandgap obtained from (a) and (b). d) The effect of pressure on Raman spectrum of highly luminescent $C_{S}Pb_{2}Br_{5}$ nanoplatelets. e) The pressure evolution of four Raman modes obtained from (d).

their frequencies change very little with pressure. We calculated the Raman phonon frequency dependence with hydrostatic pressure up to 2 GPa and the corresponding mode Grüneisen $\frac{d(\ln \omega)}{V}$, where ω is the mode frequency and V parameter $\gamma =$ d(lnV) is the unit cell volume. The DFT calculations yielded very low $\gamma_{B_{2g}}$ (69 cm⁻¹) = 0.27 and $\gamma_{A_{1g}}$ (133 cm⁻¹) = 0.23 in accordance with the weak experimentally observed frequency dependence of these modes with pressure. It is worth noting that B_{2g} (69 cm⁻¹) mode involves Pb vibrations in the basal plane resulting in out-of-phase Br_a-Pb-Br_a bending (Supporting Information)^[44] that should depend weakly on the bond angle α and consequently on hydrostatic pressure. A1g(133 cm⁻¹) mode represents Br_c stretching vibrations along the Pb-Br_c bond (Supporting Information)^[44] and the dominant change of bond angle β under pressure should have little effect on the mode frequency.

Figure 4d,e and **Figure 6** show the evolution of Raman spectra and PL of light emitting CsPb₂Br₅ nanoplatelets. Similarly to the absorption spectra evolution with pressure, the Raman features CsPb₂Br₅ remain almost the same up to 2.22 GPa. In contrast to weak responses of Raman and bandgap of CsPb₂Br₅ to hydrostatic pressure, Figure 6 reveals a drastic change of the green PL and 310 cm⁻¹ Raman band with increasing pressure: both experience significant spectral shift and diminishing intensity and eventually disappear at 2.22 GPa. The peak position of green PL decreases linearly with pressure under 1 GPa at a high rate of 50 meV GPa⁻¹. Again, these observations agree with those of CsPbBr₃ nanocrystals reported in very recent studies^[50,51] as well as in our own experiment (Figures S3–S6,







Figure 5. Calculated effects of pressure and bond length change on the band structure and bandgap of $CsPb_2Br_5$. a) Electronic band structure of $CsPb_2Br_5$ calculated at the SOC + HSE level of theory at 0 and 2 GPa. b) Bandgap energy dependence on $Pb-Br_c$ and $Pb-Br_a$ bond lengths. Blue crossed circles present the DFT results for $CsPb_2Br_5$ lattice under biaxial compressive stress and red-dot ones for axial tensile stress. The star denotes the bond length in $CsPb_2Br_5$ at 2 GPa hydrostatic pressure. The inset shows the Br atoms that occupy two nonequivalent sites in the unit cell: Br_a (in the basal (001) plane) and Br_c .



Figure 6. Pressure evolutions of associated Raman and PL spectra of the CsPb₂Br₅ nanoplatelets. a) Zoomed-in Raman spectra near 310 cm⁻¹ from Figure 4d. b–d) Evolutions of PL spectrum, PL peak position, and PL image under increasing pressure.

Supporting Information), thus confirming that green PL originates from CsPbBr₃ nanocrystals. More importantly, these observations have helped us to rule out the alternative theory of defect states due to the following reasons. For localized states such as vacancies, their state depends on the host media and their transition energy should be weakly depending on the change of host's bandgap.^[54–59] In other words, if the green PL does come from vacancy state, a presumably deep-level state based on its much smaller energy than the 3.35 eV bandgap of CsPb₂Br₅, it should experience very little spectral redshift, and should not disappear way before the possible phase transition near 4.5 GPa.

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The theory of defect states can also be excluded from the apparent observation of edge emission. If defect states such as Br vacancies are responsible for the green emission, they should be distributed evenly in the body of CsPb₂Br₅ platelets and make the whole CsPb₂Br₅ crystals bright like CsPbBr₃. The high quality of CsPb2Br5 platelets and possible attachment of CsPbBr₃ nanocrystals to their surfaces is due to their different solution growth conditions and drying process. CsPb₂Br₅ has a very low solubility in water, making them water stable, but the solubility of CsPbBr₃ is extremely high.^[17,18] As a result, CsPb₂Br₅ will always precipitate first in aqueous solution with a low initial concentration of metal halide ions. CsPbBr₃ nanocrystals will crystalize later when the solution or residues of solution dries up. This can easily happen when we convert CsPbBr3 to CsPb2Br5. For example, when we take CsPb2Br5 from the water, some solution residues will be left on their surface, most preferably on the edges, leading to the nucleation of CsPbBr₃. Because in most cases only CsPb₂Br₅ platelets with smooth surfaces or edges will be chosen for TEM, CsPbBr₃ cannot be found. The same argument and detection methods can be applied to $CsPb_2Br_5$ nanowires or nanorods.^[40,41] Because of the contamination of CsPb₂Br₅ with CsPbBr₃, we anticipate that $CsPbBr_{3-x}X_x$ (X = Cl or I) is responsible for the strong visible PL in $CsPb_2Br_{5-x}X_x$.^[19,41] This is indeed the case as can be seen from the Supporting Information where CsPb₂Br_{5-x}Cl_x nanoplatelets display similar edge emission and both their Raman and PL spectra are blueshifted compared to that of CsPb₂Br₅ due to smaller size and mass of Cl compared to Br. The opposite shifts are observed for $CsPb_2Br_{5-x}I_x$ due to larger size and mass of I.

We want to point out that many of previous studies usually underestimate the bandgap of CsPb₂Br₅ experimentally and consequently theoretically.^[28,30-33,60] One of the reasons for the experimental underestimate of optical bandgap in CsPb₂Br₅ is that the samples are PL emissive and the absorption portion of CsPbBr₃ extends the absorption tail energy in CsPb₂Br₅ down to \approx 3 eV. Our absorption measurement of nonemitting CsPb₂Br₅ gives a bandgap of 3.35 eV. This is 0.1 eV smaller than that in our HSE + SOC calculations with HSE06^[53,61] functional with incorporated screening parameter $\omega = 0.11$ Bohr⁻¹. The experimental bandgap can be reproduced exactly with $\omega = 0.13$ Bohr⁻¹ or by decreasing the Hartree-Fock exchange portion in HSE06.^[53,61] We also stress that the second order Raman band at 310 cm⁻¹ in CsPbBr₃ is much weaker than the dominant Raman lines of CsPb₂Br₅. In the case of a small amount of PL emitting CsPb₂Br₅ sample and low throughput Raman system, i.e., under conditions that do not allow measurements of a tiny fraction of impurity phases, we suggest using DAC PL alone to identify the origin of luminescent centers. Because of strong PL, DAC PL can be applied to single nanostructure or quantum dot.

In conclusion, we have revealed the root cause for the controversy over the optical properties of 2D CsPb2Br5 and its ion exchanged halides. Using a combination of two optical techniques: a static probe and a dynamic one with variable hydrostatic pressure, we successfully correlated PL with the structure one-to-one, and distinguished different mechanisms of PL from point defect versus extended structures or nanoinclusions. The bright green emission comes from CsPbBr3 nanocrystals overgrown on the surfaces, and preferably on the edges of CsPb₂Br₅ platelets, leading to bright edge emission. Because of the high stability and transparency of $CsPb_2X_5$ (X = Cl, Br, I or their mixtures) heterostructures or a mixture of CsPbX₃ with CsPb₂X₅, they have found many applications in high-efficiency LEDs and photodetectors. The resolution of this controversy opens up new opportunities to understand, design and engineer allinorganic perovskites for novel optoelectronic devices. Our integrated property-structure techniques can be applied to all optical materials to understand their emission mechanism.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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