

## SOLID-STATE FLUORESCENCE

## Under pressure



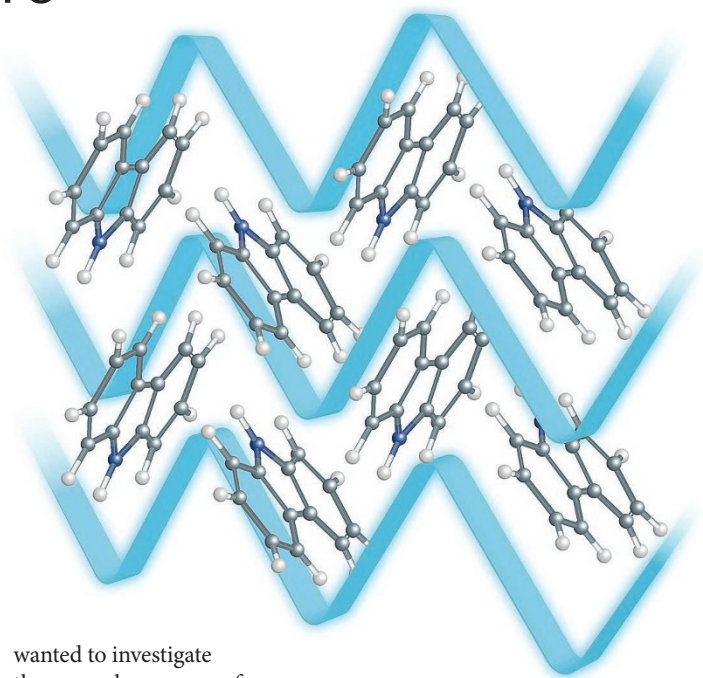
Pressure is a powerful tool to control molecular aggregation and intermolecular interactions in condensed phases, which we believe can effectively tune the emission behaviour of organic fluorophores



Aggregation-induced emission is a phenomenon in which photoemission from certain types of fluorophore is enhanced in the aggregated state. This effect can be investigated by studying the change in emission at high pressure, and now Bo Zou and co-workers provide deeper insight into the origin of pressure-induced emission enhancement in *The Journal of Physical Chemistry Letters*. Organic fluorophores are essential components of organic light-emitting diodes and light-emitting organic field-effect transistors. These applications require that the fluorophores are fabricated into solid films. However, the tendency of these molecules to aggregate in such films is the main origin of a phenomenon known as aggregation-caused quenching, which places a substantial limitation on technological developments based on fluorophores. The surprising discovery that emission from certain fluorophores can be enhanced by aggregation therefore prompted many studies into its origin.

Fluorescence can be maximized by inhibiting non-radiative energy dissipation, such as through intramolecular rotations and vibrations. “The changes in the crystal structure that are responsible for such restrictions in the molecular dynamics, however, need further study,” explains Kai Wang, a co-author of the paper. “Pressure is a powerful tool to control molecular aggregation and intermolecular interactions in condensed phases, which we believe can effectively tune the emission behaviour of organic fluorophores.”

Zou and co-workers have previously studied the role of the inhibition of intramolecular rotations for the pressure-induced emission enhancement, but in this work they



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wanted to investigate the same phenomenon for fluorophores without a rotor. They used a combination of fluorescence and IR spectroscopy, X-ray powder diffraction and electron-density distribution calculations to study the photoluminescence emission of carbazole under pressure.

Carbazole is a blue-emitting fluorophore that in the condensed phase assumes a herringbone-like structure, which is stabilized by intermolecular N–H $\cdots\pi$  and C–H $\cdots\pi$  hydrogen bonds. As the pressure is increased, the carbazole crystal undergoes structural adjustment that, at first, causes photoluminescence emission enhancement. Increasing the pressure up to 1 GPa results in a reduction of the crystal volume and a consequent enhancement of the N–H $\cdots\pi$  interactions. This increased interaction inhibits the N–H stretching vibration, which results in the limitation of non-radiative energy dissipation. At pressures higher than 1 GPa, a further reduction of

the crystal volume forces the carbazole molecules to assume a more parallel arrangement, which results in increased  $\pi$ – $\pi$  interactions and quenching of the photoemission.

“Our study provides direct experimental evidence for the link between the pressure-induced emission enhancement and the restriction of intramolecular vibrations in carbazole crystals,” explains Wang. This work offers additional fundamental insight into the essential role of intermolecular interactions in fluorescence emission. It is hoped that this will eventually facilitate the design of promising new fluorescent materials.

Gabriella Graziano

**ORIGINAL ARTICLE** Gu, Y. et al. Pressure-induced emission enhancement of carbazole: the restriction of intramolecular vibration. *J. Phys. Chem. Lett.* **8**, 4191–4196 (2017)

**FURTHER READING** Yuan, H. et al. Luminescence properties of compressed tetraphenylethene: the role of intermolecular interactions. *J. Phys. Chem. Lett.* **5**, 2968–2973 (2014)