

Design rules for organic near-infrared emitters

Margherita Maiuri

The development of high-performance organic LEDs and other devices that emit near-infrared light has been hindered by seemingly fundamental features of the light-emitting molecules. A potential solution has been identified. **See p.355**

Organic light-emitting diodes (OLEDs) are now widely used to illuminate the displays of electronic devices. Materials that radiate near-infrared (NIR) light would enable a range of desirable applications, including short-range communications and biomedical sensors. But the development of high-performance NIR OLEDs has been hindered by a fundamental problem: small molecules that emit NIR light harbour vibrations that can couple to, and thereby promote, electronic transitions that weaken the emission. On page 355, Ghosh *et al.*¹ show that this intrinsic problem can be mitigated by isolating molecular vibrations in a way that prevents them from coupling to the unwanted electronic transitions.

Light emission from a fluorescent molecule is initiated when the molecule is excited by the absorption of a photon. This results in the formation of an exciton, which is an excitation that consists of an electron paired with a 'hole' (a quasiparticle that can be thought of as the positively charged counterpart of

the electron). A photon is then emitted when the excited molecule relaxes back to the lowest-energy state.

However, non-radiative relaxation processes, which do not result in photon emission, can also occur, competing with fluorescence. Organic fluorescent molecules have high-frequency vibrations that couple to excitons in a way that accelerates non-radiative relaxation. This drastically reduces the emission quantum yield (a measure of the efficiency of photon emission), limiting the optoelectronic applications of these molecules.

The energy-gap law² predicts that non-radiative transitions between two electronic states speed up when the energy gap between the states is decreased. Molecules that absorb light in the deep red and NIR spectral regions have a small energy gap and are therefore expected to emit weakly from their lowest excited states. However, an apparent violation of the law can occur in some cases: certain organic radical molecules have high emission quantum yields

of NIR light³, for example. This is because the non-radiative relaxation rate depends not only on the energy gap, but also on the frequency of the molecular vibrations coupled to the electronic transition that promotes non-radiative relaxation². High-frequency vibrational modes promote ultrafast non-radiative processes that dominate relaxation, thus suppressing the emission quantum yield.

In this context, Ghosh *et al.* posed a pertinent question: is it possible to decouple high-frequency vibrational modes from electronic transitions to slow down non-radiative relaxation, thereby enhancing the emission quantum yield? If so, perhaps this could explain why some organic radicals are efficient NIR emitters. The authors screened organic NIR absorbers and emitters, including radicals, using a combination of ultrafast spectroscopy and quantum chemical calculations to visualize exciton–vibration coupling and to correlate that coupling with emission rates. This work answered the question in the affirmative, allowing the authors to propose two principles for designing molecules that have high emission quantum yields.

First, they proposed that when the exciton has substantial charge-transfer character – which occurs in molecules in which charge is shared between electron-donating and electron-accepting structural motifs – high-frequency vibrational modes can be localized to either the donor or the acceptor motif. This prevents those vibrations from substantially perturbing the energy and the spatial distribution of the exciton.

But charge-transfer excitons are not sufficient to ensure high-emission quantum yields. The authors conjectured that the geometrical symmetry of the molecule must also be restricted. Specifically, they posited

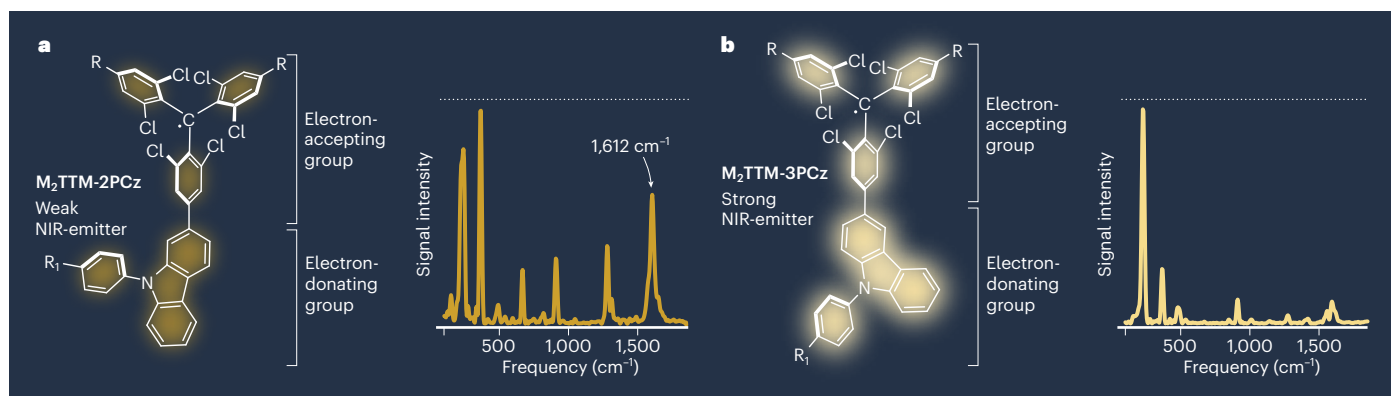


Figure 1 | How to boost near-infrared (NIR) emission from organic molecules. Ghosh *et al.*¹ report two design principles for making high-performance organic NIR emitters. First, the molecules should contain both an electron-donating and an electron-accepting group. This allows the formation of an excitation called a charge-transfer exciton (an electron paired with a quasiparticle known as a hole; not shown) and localizes high-frequency vibrations to one part of the molecule. Second, the geometrical symmetry of the molecules must result in the formation of 'non-bonding' molecular orbitals (not shown) that take part in the electronic transition responsible for

NIR emission. This helps to separate electrons and holes, and thereby prevents high-frequency vibrations from stimulating electronic transitions that compete with NIR emission. In this case, the molecule $M_2TMM-2PCz$ (a) satisfies only the first design principle, whereas the emitter $M_2TMM-3PCz$ (b) satisfies both. The vibrational spectrum of $M_2TMM-3PCz$ lacks a high-frequency peak at $1,612\text{ cm}^{-1}$, indicating that the performance-lowering effects of vibrations at that frequency have been suppressed – resulting in a high NIR emission efficiency of 94% (versus 14% for $M_2TMM-2PCz$). R, mesityl group; R_1 , C_6H_{13} . The dot on the carbon atom represents the unpaired electron of a free radical group.

News & views

that non-planar geometries associated with non-bonding orbitals – molecular orbitals that do not contribute to chemical bonding when filled by electrons – increase the separation of electrons and holes across the molecule, and thereby promote the decoupling of non-radiative transitions from high-frequency vibrations.

Ghosh *et al.* validated their design principles by preparing two new materials, both of which produced excitons with charge-transfer character, but only one of which had a molecular orbital with non-bonding character (Fig. 1). Sure enough, the combination of charge-transfer character and a non-bonding orbital resulted in strong decoupling of high-frequency vibrations, boosting the efficiency of the NIR emission quantum yield from 14% (for the compound that lacked separation) to 94%.

This is not the first attempt to bypass the energy-gap law to obtain efficient NIR emitters. Other researchers have found that OLED performance can be increased by fine-tuning the packing of emitter molecules in the solid state⁴ and by reducing the frequency of vibrations of carbon–hydrogen bonds in the molecules by

substituting the hydrogen atom with a deuterium⁵. The design principles of Ghosh and colleagues are based on observations of single molecules, but NIR emitters will be used in the solid state in future optoelectronics applications. It remains to be seen whether the principles will be affected by solid-state factors such as molecular packing or the structure of a device.

In the past decade, light-induced molecular vibrations have been reported to drive ultrafast reactions^{6–9} in several molecular systems, and even to be coupled to excitons in biological complexes¹⁰. Identifying the nature of the induced vibrational modes and unveiling their role in the rapid electronic transitions has been challenging. In most of these studies, high-frequency modes are key. Ghosh *et al.* observed vibrations with frequencies of up to 1,700 cm⁻¹ – close to the maximum frequencies that can be observed using state-of-the-art experimental techniques. The effects of higher-frequency vibrations in NIR emitters and other systems therefore currently cannot be observed. Furthermore, the specific molecular motions involved in the key vibrations remain elusive.

It will be interesting to see whether the design rules established by Ghosh and colleagues can be applied to make high-frequency vibrations enhance, rather than suppress, non-radiative transitions between excited states. This would enable the control and optimization of a range of light-induced ultrafast reactions (such as conical intersection crossings, singlet fission and electron transfers) through the design of appropriate molecules.

Margherita Maiuri is in the Department of Physics, Polytechnic University of Milan, I-20133 Milan, Italy.
e-mail: margherita.maiuri@polimi.it

1. Ghosh, P. *et al.* *Nature* **629**, 355–362 (2024).
2. Englman, R. & Jortner, J. *Mol. Phys.* **18**, 145–164 (1970).
3. Ai, X. *et al.* *Nature* **563**, 536–540 (2018).
4. Wei, Y.-C. *et al.* *Nature Photon.* **14**, 570–577 (2020).
5. Wang, S.-F. *et al.* *Nature Photon.* **16**, 843–850 (2022).
6. Falke, S. M. *et al.* *Science* **344**, 1001–1005 (2014).
7. Rather, S. R., Fu, B., Kudisch, B. & Scholes, G. D. *Nature Chem.* **13**, 70–76 (2021).
8. Musser, A. J. *et al.* *Nature Phys.* **11**, 352–357 (2015).
9. Schnedermann, C. *et al.* *Nature Commun.* **10**, 4207 (2019).
10. Maiuri, M. *et al.* *Nature Chem.* **10**, 177–183 (2018).

The author declares no competing interests.



Streamlined skull helps foxes take a nosedive

A snowy landscape offers few promises of food at first glance. However, red foxes (*Vulpes vulpes*) and Arctic foxes (*Vulpes lagopus*) can thrive in this harsh environment. These creatures can hear rodents moving beneath the surface of the snow, and use a predatory strategy of leaping into the air and diving head first (pictured) into snow to catch prey.

Slamming into snow at high speed might result in an injury unless the skull shape had evolved to minimize potential damage. As Yuk and colleagues report in *Proceedings of the National Academy of Sciences* (J. Yuk *et al.* *Proc. Natl Acad. Sci. USA* **121**, e2321179121; 2024), the skulls of animals that engage in this activity are well suited to provide protection.

The authors examined videos of this predatory behaviour in the wild, and used 3D-printed fox skulls to assess and model the forces that work on skulls dropped into fresh snow at high speed. Yuk *et al.* compared the skull shapes of the snow-diving foxes with those of other related species, and report that the sharp and elongated faces of the red and Arctic foxes help to reduce the force of impact experienced when plunging into snow.

Mary Abraham