This design principle confers that by manipulating the MW and aromatic amino acid content of a particular IDP, one can make tunable phase-separated compartments both in vitro and in cells. This is particularly important for the upcoming field of synthetic bio-condensates, which can modulate cellular functions in a controllable and designable fashion. For example, synthetic bio-condensates could be designed to modulate the functionality so that they are able to deliver bioactive drugs[6], encapsulate particular biomolecule(s) for sequestration and act as artificial catalytic centres inside cells[5]. By introducing a nuclear localization signal peptide or specific import/export sequence into these A-IDPs, it is conceivable that one could even control the localization of these condensates (nucleus or cytoplasm).

Although Chilkoti and co-workers did not show tunable phase separation in mammalian cells, similar design principles could be used in the future to precisely control the phase separation of designer or natural IDPs in mammalian cells with the help of the MW and/or mutation 'switch'. In many cases, naturally occurring IDPs undergo aberrant phase separation that eventually leads to a liquid-to-solid transition associated with diseases[7]. It will be extremely interesting if one can have control over the disease-associated solidification of condensates using expression levels, MW and/or amino acid mutation(s). Such an advance would be very relevant in understanding the sequence-specific cues that build the basic differences between functional and malfunctional (disease-associated) phase separation. ❐

**Soumik Ray and Samir K. Maji** ✉
*Department of Biosciences and Bioengineering, IIT Bombay, Powai, Mumbai, India.*
✉*e-mail: samirmaji@iitb.ac.in*

https://doi.org/10.1038/s41557-020-0532-2

## References

1. Shin, Y. & Brangwynne, C. P. *Science* **357**, eaaf4382 (2017).
2. Brangwynne, C. P., Tompa, P. & Pappu, R. V. *Nat. Phys.* **11**, 899–904 (2015).
3. Wang, J. et al. *Cell* **174**, 688–699 (2018).
4. Quiroz, F. G. & Chilkoti, A. *Nat. Mater.* **14**, 1164–1171 (2015).
5. Dizuricky, M., Rogers, A. B., Shahid, A., Cremer, S. P., Chilkoti, A. *Nat. Chem.* https://doi.org/10.1038/s41557-020-0511-7 (2020).
6. Klein, A. I. et al. *Science* **368**, 1386–1392 (2020).
7. Banani, S. F., Lee, H. O., Hyman, A. A. & Rosen, M. K. *Nat. Rev. Mol. Cell Biol.* **18**, 285–298 (2017).

## Competing interests

The authors declare no competing interests.

---

VIBRONIC COHERENCES

# The future iron age

Recent research has shown that vibronic coherences are one of the primary drivers for ultrafast light-induced processes. Now, ultrafast spectroscopy has been used to uncover vibronic coherences in the excited-state dynamics of an iron complex, leading to its redesign and the drastic prolonging of its excited-state lifetime.

Julia A. Weinstein

Society uses light-driven applications everywhere and every day, and chemists across the world are working to understand, control and ultimately improve many of them. But the molecular response to light can be very complex, and thus so can tailoring light-driven properties.

Absorption of light is ultrafast — femtoseconds, if that — and those very first moments during which a molecule's excited electronic states are populated determine much of what happens afterwards: the nature and yield of the reaction products, the efficiency of light harvesting or the photostability of the material. Over the past few decades, with the advent of ultrafast optical methods, and more recently ultrafast X-ray-based methods, several scientific areas have emerged that explore the possibility of influencing these excited states and the accompanying electronic, spin and structural properties.

Recent elegant research using primarily electronic and two-dimensional spectroscopies has explored quantum-mechanical 'coherences' in light-driven processes[1], seeking to understand and manipulate function in a variety of systems — from molecules to photosynthetic structures. This work, along with the recent application of mode-specific vibrational excitation to manipulate excited states in solution[2], has highlighted the special role that vibrations can play on the ultrafast timescale, when the Born–Oppenheimer approximation is not applicable. In such systems, multiple electronic and nuclear degrees of freedom are convolved, electronic and vibrational wavefunctions are mixed, and vibronic wavepackets emerge that drive photophysical processes. Such vibronic coherence can become the determining contributor to the reaction dynamics — and could dictate the preferred reaction pathway.

Now, as described in *Nature*, McCusker and co-workers have used their understanding of vibronic coherences in the excited-state dynamics of an iron-based chromophore to redesign its structure and tune its function[3]. Their strategy relied on them identifying vibrations that are coupled to the decay of the chromophore's excited state and stopping them by making changes to the molecule's structure. This seemingly simple solution is excruciatingly difficult to execute — how does one identify such vibrations in the dynamic landscape when multiple degrees of freedom are coupled? And, even if excited-state dynamics could be controlled like this, how could the fundamental knowledge acquired be translated into improved function, for example, in light-driven applications?

Transition-metal complexes of Ru, Ir, Re and Pt are important for such solar applications. They have all the properties necessary for harnessing the energy of light: strong absorption of visible light, relatively modular design and long-lived excited states of charge-transfer nature, usually a metal-to-ligand charge transfer (MLCT) state. Ultrafast, subpicosecond intersystem crossing from the initially populated excited state to the triplet manifold leads to $^3$MLCT states with lifetimes of hundreds of nanoseconds or longer. These transition metals, however, are rare and expensive and replacing them with one of their first-row analogues would be very important from an applied and industrial standpoint. Yet excited states in complexes of first-row transition metals have lifetimes millions of times shorter than those of third-row

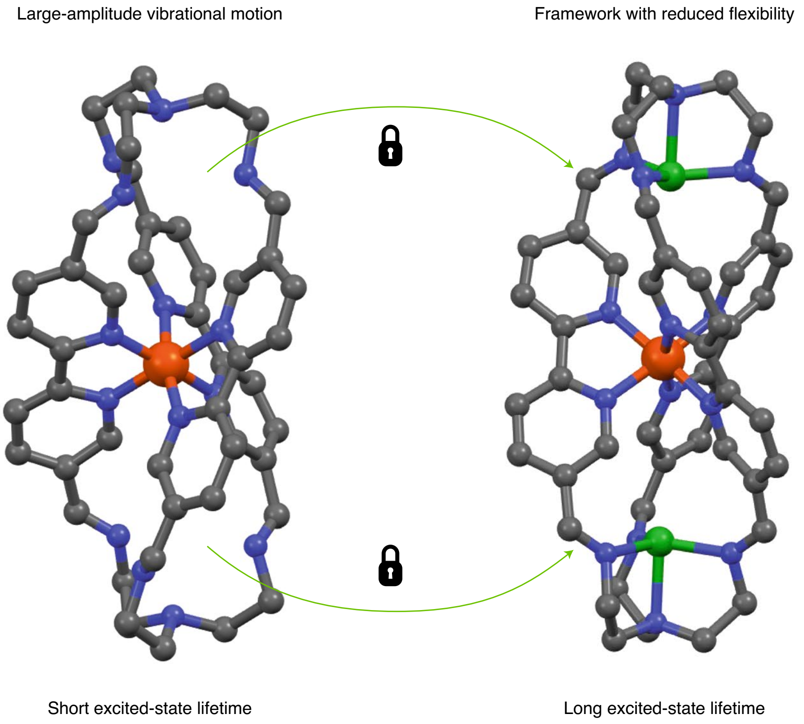

**Fig. 1 | Restricting vibrations leads to a longer excited-state lifetime.** A rendering of the Fe(II) bipyridine complex with a 'floppy' frame — and thus a short excited-state lifetime — is on the left and the complex with the same core, but made more rigid through the addition of copper atoms, is on the right. 'Locking' the ligand framework, that is, making it more rigid, alters the dynamics of the excited state, increasing its lifetime. The coloured spheres represent: grey, carbon; blue, nitrogen; orange, iron; green, copper.

metals — under 300 fs in $[Fe(bpy)_3]^{2+}$ versus greater than 300 ns for the archetypal photoredox reagent, $[Ru(bpy)_3]^{2+}$ (where bpy is 2,2′-bipyridine). The reasons behind these differences are largely due to an MLCT state decaying into lower-lying *d*–*d* state(s) and accompanying large structural distortions.

A very successful strategy to increase the excited-state lifetime in Fe(II) complexes is to change the nature of the lowest excited state from an MLCT state in $[Fe(bpy)_3]^{2+}$ to a ligand-to-metal charge-transfer state, which has lifetimes as long as nanoseconds[4], and to use strong-field ligands such as heterocyclic carbenes to raise the energy of the *d*–*d* state[5].

McCusker and co-workers suggest a different strategy, one that capitalizes on the ultrafast decay of MLCT states in diimine Fe(II) complexes and builds on existing knowledge of the large changes in Fe–N bond lengths and torsional angles occurring as the excited state evolves[6,7]. They study a carefully designed complex of iron(II), which maintains three bipyridyl ligands; however, these ligands are linked into a macrocycle (Fig. 1, left).

They used femtosecond transient absorption spectroscopy to study the excited-state decay of this complex and identified a set of coherent oscillations superimposed on the kinetics. Their analysis revealed dephasing times associated with these oscillations — each in the range from 230 to 730 fs — that they classified as vibronic. This was on the basis that electronic coherence dephasing times are generally assumed to be sub-100 fs, while purely vibrational dephasing times are likely to lie in the picosecond domain[1]. Next, McCusker and co-workers, on the basis of comparisons with related Fe(II) complexes[6,7] and density functional theory calculations, determined the vibrational motions associated with the vibronic coherences.

Armed with this information, McCusker and colleagues hypothesized that they could increase the lifetime of the excited state by locking these motions. This was achieved relatively easily because the macrocyclic ligand used has additional coordination sites that, if occupied, reduce flexibility, giving some control over the molecular motions in the excited state. Thus, they coordinated additional 'innocent' Cu(I) atoms — which would not take part in light absorption or charge transfer — to the free N atoms of the scaffold (Fig. 1, right). They discovered that making the scaffold around the iron centre more rigid greatly reduces the amplitude of one of the low-frequency oscillations participating in the excited-state dynamics, and increases its dephasing time to around 700 fs. They take these two observations as an indication that the mode is becoming decoupled (at least partially) from the active reaction coordinate. The lifetime of the MLCT excited state becomes 2.6 ps — some 20 times larger than in the more flexible original structure without Cu(I).

While still very short compared with the charge-transfer states in Ru(II), Re(I) and several other metal complexes (hundreds of nanoseconds), this is the longest lifetime for a MLCT state in an Fe(II) polypyridyl complex so far. But the main contribution of the paper is more fundamental — and lies in the demonstration that ultrafast transient absorption data, using equipment that is available in many labs worldwide, can not only provide vital information on which vibrations are involved in complex excited-state decay processes but also inform molecular design to tune them.

Future developments in X-ray sciences will allow us to create even better molecular movies, and one day obtain such information directly[8]. At present, quantum coherence revealed by optical methods can enable one to engineer molecules and materials with specific properties — and get us one exciting step closer to understanding how the magic of the ultrafast world works. ❐

**Julia A. Weinstein** ✉
*Department of Chemistry, University of Sheffield, Sheffield, UK.*
✉*e-mail: julia.weinstein@sheffield.ac.uk*

https://doi.org/10.1038/s41557-020-0531-3

## References

1. Scholes, G. D. et al. *Nature* **543**, 647–656 (2017).
2. Delor, M. et al. *Science* **346**, 1492–1495 (2014).
3. Paulus, B. C. et al. *Nature* **582**, 214–218 (2020).
4. Kjær, K. S. et al. *Science* **363**, 249–253 (2019).
5. Kunnus, K. et al. *Nat. Commun.* **11**, 634 (2020).
6. Consani, C. et al. *Angew. Chem. Int. Ed.* **48**, 7184–7187 (2009).
7. Lemke, H. T. et al. *Nat. Commun.* **8**, 15342 (2017).
8. Wernet, P. *Phil. Trans. A* **377**, 20170464 (2019).

## Competing interests

The author declares no competing interests.