

Using synthesis to steer excited states and their properties and functions

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The nature, properties and reactivities of ground-state molecules have been studied widely. By contrast, the parallel manipulation and knowledge of molecules in their excited states are not well controlled or understood. Here we have investigated the manipulation and control of excited-state molecules, with the generation of libraries of molecules. The power and ability of light to drive chemical reactions, conformational changes, motion, luminescence and energy conversions in nature have inspired researchers to harness excited states to achieve the desired control of manipulation of molecules in their excited state to tackle challenges in materials and energy research and sustainability. To this end, synthesis can be used to harness excited states and molecular functional materials. Furthermore, supramolecular chemistry can provide an additional dimension of control to the excited states and expand the library of excited-state functional materials. By mastering the design of excited states, an in-depth understanding and discovery of excited states with desirable properties and controllable transformation by design may open up a new area of research, resulting in libraries of excited-state molecules and chemistry that parallel ground-state chemistry and, in doing so, offer unlimited opportunities.

The beauty of chemistry lies in its unique ability to create and manipulate molecules, as well as master their reactivity and properties. Synthetic chemistry is the powerhouse driving the chemical transformations and toolboxes behind the scenes. Alongside other disciplines within and outside chemistry, synthetic chemistry offers possibilities to steer the world towards a better way of living by addressing the challenges of the United Nations (UN) Sustainable Development Goals (SDGs), challenges that require interdisciplinary and global efforts. The COVID-19 pandemic has affirmed that scientific contributions to the development of drugs, treatments, diagnostics and preventive measures through collaborative efforts are key to addressing health-related issues for the betterment of humankind.

Equally crucial to enabling better living are functional materials, which are required for a range of uses such as energy transformation and storage, coupled with consideration of environmental issues and sustainability. For example, functional molecular materials have propelled forward the fabrication of electronics and optoelectronics on flexible, large-area substrates by means of simple processing

techniques such as sublimation, vapour deposition, vapour-jet deposition, spin-coating, inkjet printing and roll-to-roll printing. This processability has been realized by the discovery of evaporable organic and metal-organic small molecules, as well as solution-processable organic and metal-organic molecules, dendrimers, oligomers and polymers. These molecules and macromolecules are very different from the inorganic semiconductors that make up conventional electronics and optoelectronics. Together with the advantages of the processability of molecular materials, the ease of tunability of their properties by rational molecular design via the rich diversity and versatility of synthetic routes and the control of the nature of frontier molecular orbitals and their energies have led to organic electronics and optoelectronics, such as organic thin-film transistors (OTFTs), organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs) and sensors, as well as smart materials with desirable properties and promising functions and performances.

Luminescent or light-emitting materials for OLEDs, or strongly light-absorbing materials for light-harvesting, photosensitization,

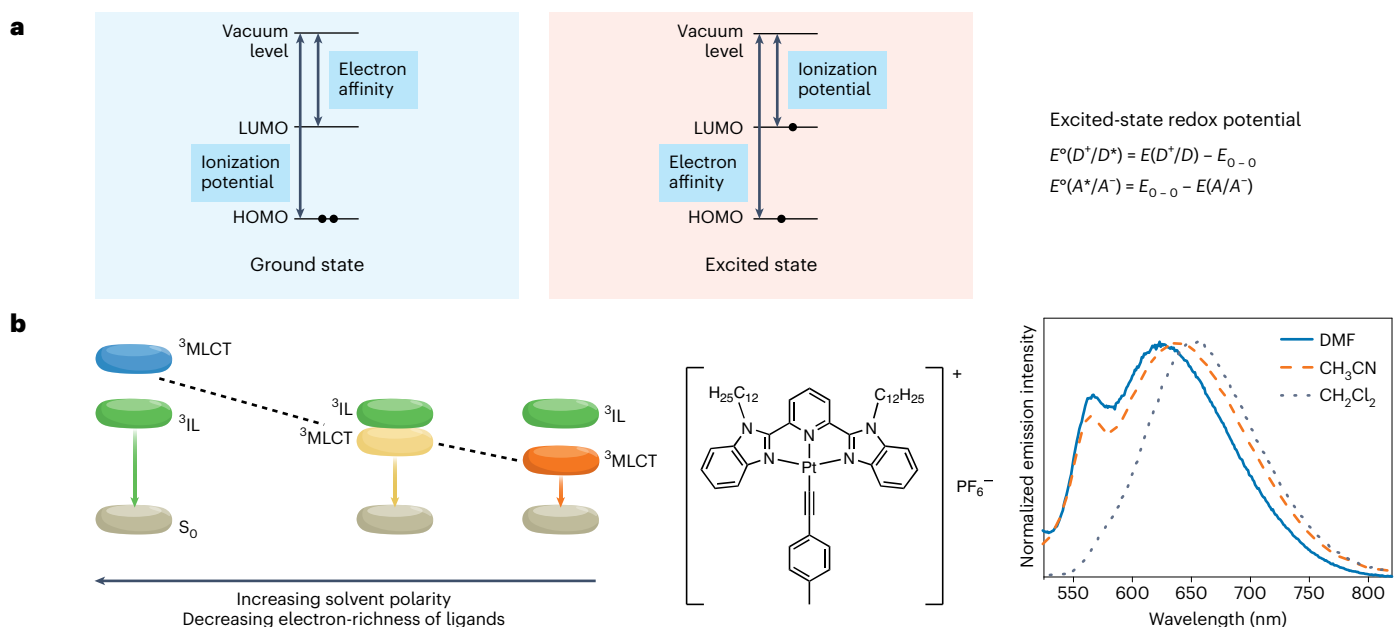


Fig. 1 | Excited-state properties. **a**, Simplified molecular orbital energy level diagram demonstrating the different oxidizing and reducing powers of the ground state and excited state, and the determination of the excited-state redox potential. **b**, Left: change of nature of excited states through ligand design and microenvironment. Middle: chemical structure of $[\text{Pt}\{(\text{C}_{12}\text{H}_{25})_2\text{bzimpy}\}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-(\text{CH}_3)_4)]\text{PF}_6$. Right: normalized emission spectra of $[\text{Pt}\{(\text{C}_{12}\text{H}_{25})_2\text{bzimpy}\}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-(\text{CH}_3)_4)]\text{PF}_6$ in DMF, CH_3CN and CH_2Cl_2 at room temperature.

bzimpy, 2,6-bis(benzimidazol-2'-yl)pyridine; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital, E_{0-0} , zero-zero spectroscopic energy; $E^{\circ}(D^{\bullet}/D^{\bullet+})$ and $E^{\circ}(A^{\bullet}/A^{\bullet-})$, excited-state redox potentials for oxidative and reductive electron-transfer quenching, respectively; $E(D^{\bullet}/D)$ and $E(A/A^{\bullet})$, ground-state redox potentials; MLCT, metal-to-ligand charge transfer; IL, intraligand; S_0 , ground state; DMF, dimethylformamide. Panel **b** adapted with permission from ref. ²⁰, Wiley.

solar conversion and OPVs, or photocatalysts have in common the involvement of a light-enabling function. In the design of such materials, the excited state is key to success. An excited-state molecule can be considered as a new chemical species because it can, in most cases, have a different electronic configuration or sometimes adopt a different intraconfigurational spin state, a different structure, different properties and different reactivity from those of the ground state. One can use synthesis to change the energy levels, the order of the molecular orbitals, the electronic communication, and the nature and spectroscopic origin of the excited states. These permit the design of different luminescent materials with different emission characteristics and efficiencies—essentially using synthesis to harness excited states and molecular functional materials.

Molecules in their ground state have been widely studied, as have their manipulation and control, leading to huge libraries of molecules and their molecular properties and reactivities. However, the parallel manipulation and knowledge of molecules in their excited states is not as well defined or understood. By mastering the design of excited states, an in-depth understanding and discovery of excited states with desirable properties and controllable transformation by design may open up a new area of research. The realm of excited states has the potential to offer a library of new excited-state chemical species and excited states that parallel ground-state chemistry, with unlimited opportunities and a wealth of excited-state functional materials and chemistry to be exploited. Moreover, for the same chemical species, there can be more than one excited state, each with a different nature, energy, structure and reactivity, thus opening up an infinite library of excited-state species, each with unique and characteristic properties and reactivities.

Control of the nature of excited states

To illustrate the importance of the nature of excited states and the control of excited-state properties and their associated excited-state

reactivities, we first examine metal complexes with metal-to-ligand charge transfer (MLCT) excited states. The classical $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with a low-spin d^6 electronic configuration of the metal centre and 2,2'-bipyridine (bpy) π -acceptor ligands provides an example of an MLCT excited state following photoexcitation^{1,2}. The bpy ligand has a relatively low-energy, empty π^* antibonding orbital. The orange emission of $[\text{Ru}(\text{bpy})_3]^{2+}$ is a phosphorescence originating from a triplet MLCT ($^3\text{MLCT}[d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{bpy})]$) excited state. Attaching electron-donating substituents onto the bpy ligand raises the energy of the ligand π^* orbital to give a higher-energy emission maximum at shorter wavelengths, whereas attaching electron-withdrawing substituents on the bpy ligand shifts the emission wavelength maximum to the red. Besides the MLCT excited state, $[\text{Ru}(\text{bpy})_3]^{2+}$ also possesses a $d-d$ ligand-field (LF) excited state that originates from the promotion of an electron from the non-bonding $d_{\pi}(\text{Ru})$ orbital to the antibonding $d_{\sigma}^*(\text{Ru})$ orbital³. The observation of phosphorescence from the $^3\text{MLCT}[d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{bpy})]$ excited state stems from the lower-lying energy of the $^3\text{MLCT}[d_{\pi}(\text{Ru}) \rightarrow \pi^*(\text{bpy})]$ excited state rather than the triplet ligand-field $^3\text{LF}[d_{\pi}(\text{Ru}) \rightarrow d_{\sigma}^*(\text{Ru})]$ excited state, because the emission from most luminescent compounds originates from the lowest-energy excited state³, mainly governed by Kasha's rule, although examples of anti-Kasha's rule have been observed recently.

A simple synthetic modification of $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ leads to the absence of emission and an ejection of the pyridine (py) ligand upon light excitation⁴. Such a replacement of the bpy ligand with two monodentate py ligands reverts the energy order of the $^3\text{MLCT}$ and ^3LF excited states, causing the ^3LF excited state to become the lowest-energy excited state. As the energies of the two excited states of different nature are reversed, rapid non-radiative decay or internal conversion from the higher-lying $^3\text{MLCT}$ state to the lowest-energy ^3LF state leads to characteristics and reactivities typical of the ^3LF excited state. The ^3LF state involves excitation of an electron from a non-bonding $d_{\pi}(\text{Ru})$ orbital to the $d_{\sigma}^*(\text{Ru})$ orbital, which is antibonding

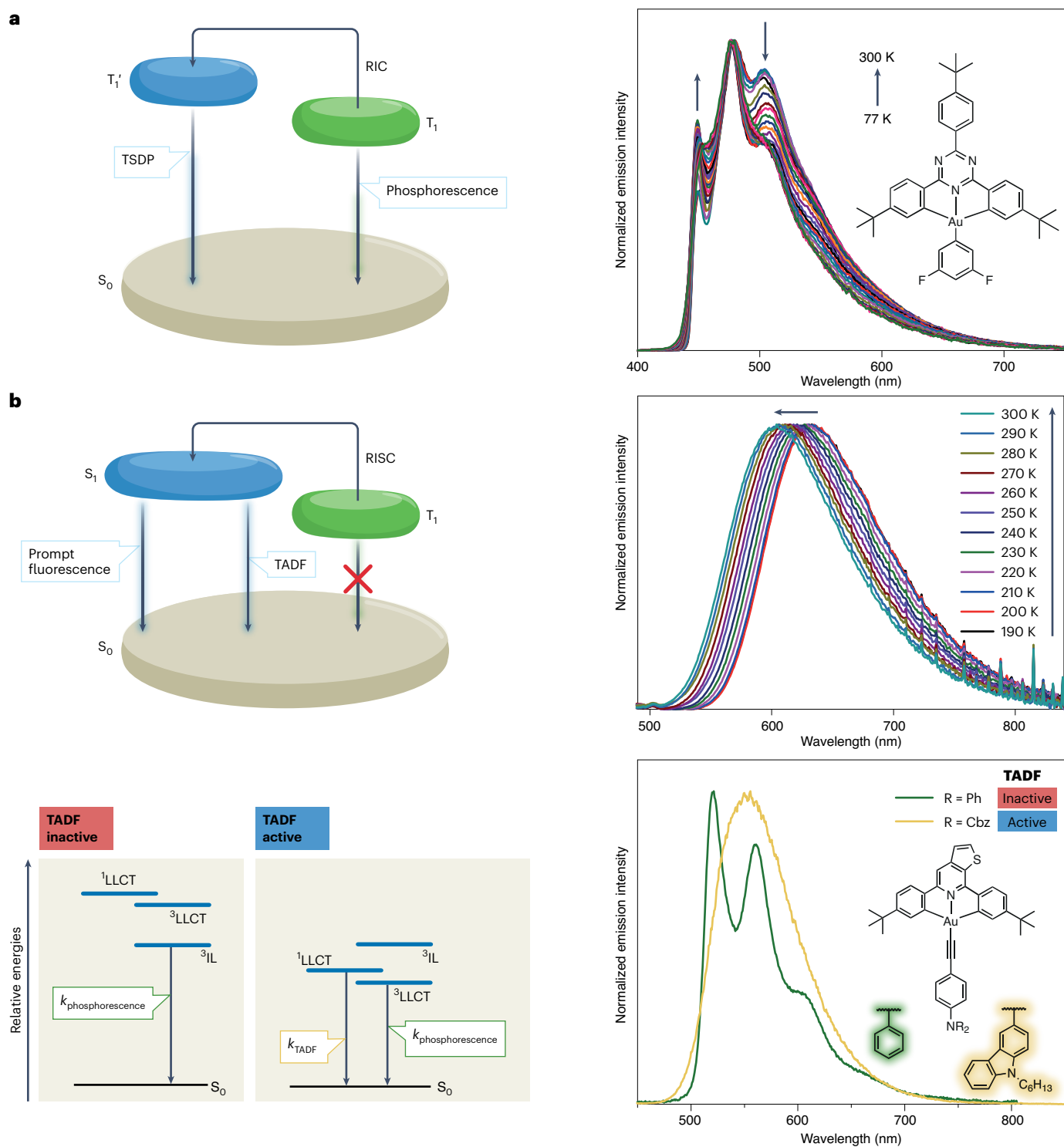


Fig. 2 | Thermally activated processes. **a**, Left: thermally stimulated delayed phosphorescence (TSDP). Right: normalized solid-state emission spectra of an arylgold(III) complex at different temperatures between 77 and 300 K upon excitation at 360 nm. **b**, Top left: thermally activated delayed fluorescence (TADF). Top right: normalized emission spectra of an alkynylgold(III) complex in degassed toluene upon increasing temperature from 190 to 300 K. Bottom left: qualitative state diagram depicting the relative energies of the $^1\text{LLCT}$ states and the ^3IL state of alkynylgold(III) complexes in the solid state at 298 K, showing the

differences in the excited states that lead to distinctive TADF properties. Bottom right: normalized emission spectra of alkynylgold(III) complexes in 5 wt% doped 1,3-bis(*N*-carbazolyl)benzene (mCP) thin films at 298 K showing different origin in the emissive excited states. RIC, reverse internal conversion; RISC, reverse intersystem crossing; S_0 , singlet ground state; S_1 , singlet excited state; T_1 , T_1' , triplet excited state; LLCT, ligand-to-ligand charge transfer; IL, intraligand; k , radiative rate constants; Ph, phenyl; Cbz, *N*-hexylcarbazolyl. Figure adapted with permission from: **a**, ref. ²¹, American Chemical Society; **b**, ref. ²³, RSC.

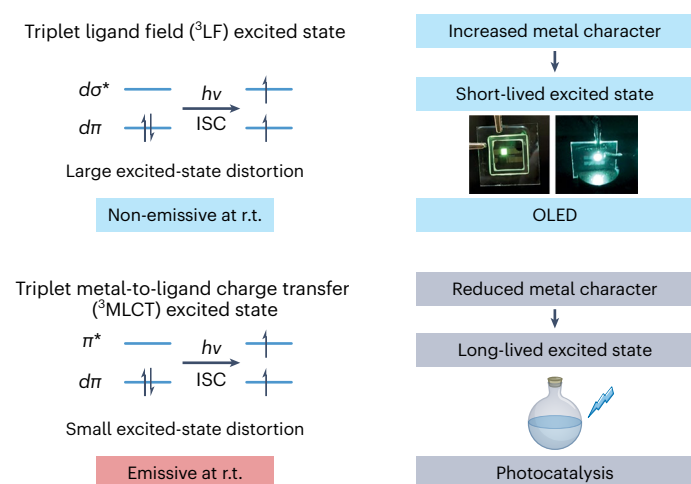


Fig. 3 | The nature of excited states and their properties and functions.

Left: the excited states and their properties and reactivities, as well as the manipulation of the lifetimes of excited states for different functions. Right: applications of short-lived (top) and long-lived (bottom) excited states into OLED (top) and photocatalysis (bottom) applications. RT, room temperature; ISC, intersystem crossing; OLED, organic light-emitting diode; $h\nu$, light excitation.

with respect to the Ru–N bond, and, as a result, a large excited-state structural distortion with lengthening and weakening of the Ru–N bond takes place, lowering the activation barrier for the rupture of the Ru–N bond with the leaving of the py ligand. Such a highly distorted structure in the excited state also dissipates its excess excited-state energy via non-radiative vibrational modes and bond breaking, leading to the lack of room-temperature emission⁴.

Capitalizing on the photo-substitution reactivity of ³LF excited states, photo-release and photo-delivery systems for small molecules such as NO and CO (photoCORM), for biological applications, have been designed using low-spin d^6 metal complexes of Ru(II), W(0), Mn(I) and d^3 Cr(III) with low-lying ³LF excited states⁵. By contrast, ³MLCT excited states are well known for undergoing photoredox reactions given the charge-transfer nature of the excited state. This has been facilitated by the stronger oxidizing and reducing power of the ³MLCT excited state than the ground state, as reflected by the excited-state redox potentials, as well as the facile electron-transfer kinetics associated with their facile self-exchange rate constants^{6,7}, which are favoured both thermodynamically and kinetically. The thermodynamic aspect is illustrated in Fig. 1a, where E_{0-0} is the zero–zero spectroscopic energy and $E^{\circ}(D^+/D^*)$ and $E^{\circ}(A^+/A^*)$ are the excited-state redox potentials for oxidative and reductive electron-transfer quenching, respectively, which can be estimated assuming a negligible entropy change between the excited state and the ground state (Fig. 1a). The photoredox reactivity of the ³MLCT excited state has been increasingly exploited for photoredox catalysis, as exemplified by [Ru(bpy)₃]²⁺ and the related d^6 Ir(III) complex, [Ir(ppy)₃] (Hppy = 2-phenylpyridine)⁸.

Interplay of excited states

Apart from the classical octahedral MLCT complexes of Ru(II), Re(I) and Ir(III) diimines or ppy derivatives^{1–4,9,10}, square-planar metal complexes with a d^8 electronic configuration, especially those of Pt(II), are unique^{11–20}. By introducing highly soluble and strongly electron-donating alkynyl ligands to the Pt(II) polypyridine system, it is possible to enrich their excited-state properties by introducing an alkynyl-to-polypyridine ligand-to-ligand charge transfer (LLCT) excited state, or sometimes an LLCT excited-state character, into the MLCT excited state^{17–19}. With appropriate choice of the polypyridine, such as the bidentate bpy or tridentate 2,2':6',2''-terpyridine (terpy) or 2,6-bis(benzimidazol-2'-yl)pyridine (bzimpy) pincer ligands, fine control of the nature of the

lowest-lying excited state can be readily realized^{14,15,17–20}. For example, with the use of a ligand with intraligand (IL) $\pi-\pi^*$ excited-state energy that is lower lying than that of the terpyridine counterpart, such as bzimpy, vibronic-structured ³IL emission can be observed^{17–20}. The closeness of the energies of the ³IL($\pi-\pi^*$) excited state and ³MLCT [$d_{\pi}(\text{Pt}) \rightarrow \pi^*(\text{bzimpy})$]/³LLCT [$\pi(\text{alkynyl}) \rightarrow \pi^*(\text{bzimpy})$] admixture excited state can lead to dual luminescence. A simple modification of the electronic properties of the ligands and the polarity of the solvents can perturb the relative energies of the two excited states given the sensitivity of the CT state to the electronic properties of the alkynyl ligands and the solvents, with the negative solvatochromic behaviour exhibited by these platinum(II) complexes, as well as the closeness of the energies of the ³IL and ³CT states that can lead to the ready tunability of the nature of the emissive states²⁰. For example, the use of a less polar solvent or a more electron-rich alkynyl ligand will preferentially stabilize the ³MLCT/LLCT state to become the lowest-lying excited state responsible for emission, leading to the observation of a Gaussian-shape structureless emission band of ³MLCT/LLCT origin. On the contrary, the use of a less electron-rich alkynyl ligand or a more polar solvent will raise the energy of the ³MLCT/LLCT states, rendering the ³IL excited state lower lying in energy, leading to the observation of a vibronic-structured ³IL emission band with a long excited-state lifetime²⁰ (Fig. 1b).

Thermally activated excited states

The closeness in the energy of two close-lying excited states that are neither fully coupled nor fully orthogonal can be exploited for thermally activated luminescence processes. With rational design, introduction of an appropriate aryl group to the central triazine unit of the cyclo-metalating diaryl-triazine (C[∧]N[∧]C) ligand in Au(III) complexes has led to the introduction of a lower-energy triplet intraligand charge transfer (³ILCT) excited state in addition to a ³IL [$\pi-\pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})$] excited state^{21,22}. By controlling the dihedral angle between the aryl substituent and the central triazine unit and hence the conformation, the energy gap between the lower-lying green-emitting ³ILCT excited state (T_1) and the higher-energy blue-emitting ³IL [$\pi-\pi^*(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})$] excited state (T_1') can be perturbed to influence the efficiency of upconversion from the T_1 to T_1' state via spin-allowed reverse internal conversion (RIC), giving rise to thermally stimulated delayed phosphorescence (TSDP) from the higher-energy T_1' excited state to give blue emission^{21,22} (Fig. 2a). Such a design strategy can overcome some of the challenges associated with blue emitters, which are typically less photochemically robust given the presence of highly energetic blue excitons. These excitons may undergo exciton–exciton annihilation to generate energies as high as over 5 eV, and are sufficient to rupture a chemical bond. The lower-lying T_1 state can serve as a resting state that offers higher photostability, which on upconversion gives blue emission, while at the same time serving as a buffer or mediator to capture any exciton loss from the higher-lying T_1' state owing to non-radiative decay, and recycling it back from the T_1 state to the T_1' state to enhance its photoluminescence quantum yield (PLQY)^{21,22}. Interestingly, the sensitivity of the ³ILCT state to the conformation of the aryl ring relative to the C[∧]N(triazine)[∧]C pincer ligand has led to control of the turning on or turning off of RIC and TSDP and the mechanoluminescence behaviour of the emission colour in pristine crystals versus the powder generated by mechanical grinding^{21,22}.

Parallel to TSDP, thermally activated delayed fluorescence (TADF) emitters, involving upconversion via spin-forbidden reverse intersystem crossing (RISC), can be obtained through molecular design to perturb the spin–orbit Hamiltonian and the electronic coupling and thus provide good separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the donor–acceptor-type emitters, allowing TADF to occur²³ (Fig. 2b). The TADF phenomenon, revisited by Adachi for the development of TADF OLEDs based on organic molecules²⁴ and by Yersin based on Cu(I) TADF materials²⁵ to harvest both singlet and triplet excitons, has attracted growing attention. Interestingly, the switching of the energy order of

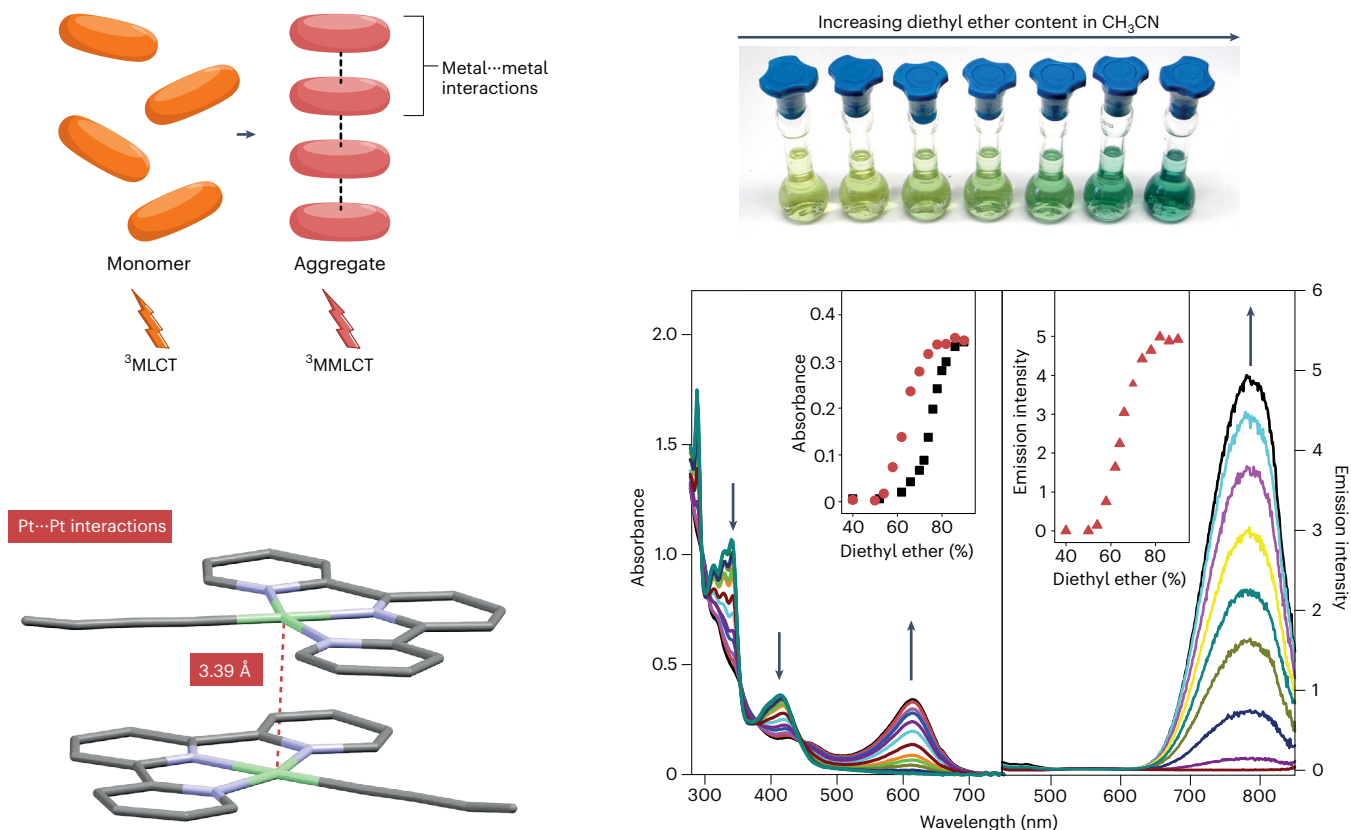


Fig. 4 | An additional dimension of excited-state control through supramolecular assembly. Top left: a schematic representation showing the difference between monomer and aggregate using metal–metal interactions as an additional driving force for the aggregation. Top right: a photograph showing the changes in solution colour of the CH_3CN solution of $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ upon the addition of diethyl ether. Bottom left: X-ray crystal structure of $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ showing $\text{Pt}\cdots\text{Pt}$ interactions. Bottom right: ultraviolet–visible absorption changes of $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ (concentration = 1.47×10^{-4} M) in CH_3CN with increasing diethyl ether content

(left). Emission enhancement of $[\text{Pt}(\text{terpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ (concentration = 1.47×10^{-4} M) in acetone with increasing diethyl ether content (right). Inset (left): plot of absorbance as a function of diethyl ether composition in CH_3CN at 615 nm (black) and in acetone at 610 nm (red). Inset (right): plot of corrected emission intensity as a function of diethyl ether composition. terpy, 2,2':6',2''-terpyridine; OTf, trifluoromethanesulfonate; MLCT, metal-to-ligand charge transfer; MMLCT, metal–metal-to-ligand charge transfer. Figure adapted with permission from ref. ²⁷, American Chemical Society.

LLCT versus IL excited states by varying the electron–donor strength of the auxiliary alkynyl ligand can lead to turning-on or turning-off of the TADF activity (Fig. 2b).

Manipulation of excited states by metals

Interestingly, the effect and nature of the metal play an important role in reducing the excited-state lifetime of not only phosphorescent materials, but also TADF emitters, by enhancing the efficiency of spin–orbit coupling. Depending on the functional properties that are desired, the lifetime requirement of the excited state can vary a lot. Luminescent materials for OLED applications should not have overly long excited-state lifetimes, because long-lived excitons, such as triplet excitons, are susceptible to triplet–triplet or exciton–exciton annihilation as well as exciton–polaron annihilation, which leads to large efficiency roll-offs and device degradation²⁶. For example, a larger mixing of metal character will lead to both the harvesting of singlet and triplet excitons and shorter-lived excited states, which are advantageous to OLED materials design. However, excited states for bimolecular photochemical reactions and photocatalysis need to live long enough to have sufficient time to interact with their reaction partners and the substrates of interest and thus for the photochemical reactions to occur (Fig. 3).

Excited-state control via supramolecular assembly

What is more interesting is that the square-planar geometry of d^8 Pt(II) and Rh(I), and more recently Au(III), Pd(II) and Ni(II), as well as the linear

or trigonal planar geometry of d^{10} Au(I) have provided an additional dimension to harness the nature and energy of excited states^{17,22,27–32}. The facility of these square-planar, linear or trigonal planar complexes to stack and aggregate, and form a supramolecular assembly, will have an impact on the excited states. The ability of these low-dimensional metal complexes to assemble through non-covalent intermolecular forces of π – π stacking interactions, electrostatic interactions, hydrophobic interactions and, especially for Pt(II), Rh(I) and Au(I), significant metal–metal interactions, has provided the opportunity to control molecular packing, alignment, orientation and assembly, as well as molecular conformation and topology to promote excitonic coupling. Such coupling gives excited-state properties, such as absorption and emission as well as reactivity, characteristic of the excimers, dimers, oligomers and the rigid aggregates, usually with redshifted absorption and emission colours, higher PLQY and lower susceptibility to oxygen quenching^{17,27–32} (Fig. 4). The anisotropic directionality of the non-covalent metal–metal interactions has provided a good handle to enable control over how molecules pack, align and self-assemble in the fabrication of functional molecular materials, via manipulation of the delicate balance of the various non-covalent intermolecular forces that hold the molecules together, as well as the intramolecular forces that govern molecular conformation, topology, as well as the morphology^{17,28,29}. Such supramolecular control, together with the expansion of the already diverse libraries of molecules through the power of synthesis as well as the generation and harnessing of their

excited states, will create unlimited exciting opportunities for breakthroughs in luminescence, photocatalysis and light-enabled functions.

Outlook

Light is an invaluable and plentiful source of energy. The power and ability of light to drive chemical reactions, conformational changes, motions, luminescence and energy conversions in nature have inspired researchers to harness excited states to achieve desirable control of the manipulation of molecules in their excited state to tackle challenges in materials and energy research and sustainability. By mastering the design of excited states, an in-depth understanding and discovery of excited states with desirable properties and controllable transformation by design may open up a whole new area of research with new libraries of excited-state molecules and chemistry that parallel ground-state chemistry, with unlimited opportunities.

Through rational design and synthesis, various metal–ligand chromophores can be generated and readily tuned to control the energy levels and energy, the order of the molecular orbitals, electronic communication, and the nature and spectroscopic origin of the excited states, to turn on or turn off the properties and reactivities characteristic of the various excited states, such as IL, MLCT, LMCT, LF states and excited states associated with metal–metal interactions such as MMLCT states. Selected photoexcitation can be made to bring about bond dissociation or cleavage, especially through LMCT or LF excited states, for the activation of photocatalysis. Excited-state control via supramolecular assembly has provided an additional dimension to harness the nature and energy of the excited states associated with control of molecular packing, alignment, orientation and assembly, as well as molecular conformation and topology. The power of synthesis to generate and harness excited states has provided unlimited opportunities for breakthroughs, leading to an infinite library of excited-state species, each with its unique and characteristic properties and reactivity.

To further demonstrate the power of chemistry and molecular science and to increase the impact of chemistry in solving global challenges, we need to look at things from a broad and holistic perspective, to learn and understand more about areas outside our main expertise and comfort zones, to develop a common language to communicate with researchers from other disciplines, and to collaborate and work in interdisciplinary areas of research, while at the same time building a solid foundation and making breakthrough discoveries in our own core discipline so as to contribute to the betterment of humankind.

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Competing interests

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Additional information

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