

## EMISSIVE MATERIALS

## OLEDs: rotation propels crossing

“Unlocking blue could have a huge impact on the display and lighting industries, finally making large-area, efficient OLED light sources a reality”



If you are reading this article on an electronic device, the chances are that you are benefitting from organic light-emitting diode (OLED) technology. Emissive materials in OLEDs undergo excitation from their singlet electronic ground state ( $S_0$ ) to either their first excited triplet ( $T_1$ ) or singlet ( $S_1$ ) states. Although the  $T_1$  state is dark,  $S_1$  relaxes to the ground state ( $S_1 \rightarrow S_0$ ) through fluorescence, a rapid spin-allowed process that is desirable for electronics applications. A problem with present emitters in OLEDs is that three-quarters of their excitation events result in promotion to the  $T_1$  state, from which intersystem crossing (ISC; here,  $T_1 \rightarrow S_1$ ) is unlikely. Yet, this transition, and the fluorescence that follows, is enabled by conformational dynamics in carbene amido complexes of copper and gold as described in *Science* by

a team led by Dan Credgington, Manfred Bochmann and Mikko Linnolahti.

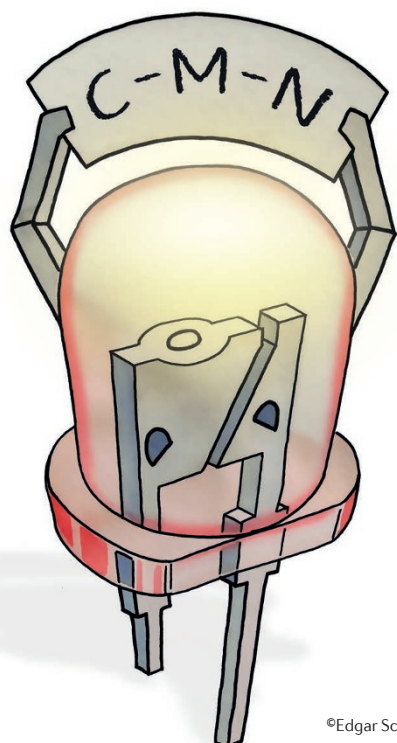
The fabrication of low-latency, durable devices requires an OLED material to make quick use of its  $T_1$  excited state, which might otherwise undergo deleterious bimolecular reactions, particularly when in densely packed arrays and when it is high in energy (as would be required if blue light is desired). Technological applications exploit the  $T_1$  state through phosphorescence ( $T_1 \rightarrow S_0$ ), a process facilitated by spin-orbit coupling in complexes of heavy metals, such as Ir, Pt or Os. Another way of harnessing the  $T_1$  state is to effect ISC by thermal upconversion, allowing the resulting  $S_1$  state to fluoresce. These two approaches are not fast (emission times are  $>1 \mu\text{s}$ ), and are not amenable to emitting blue light, motivating Credgington and co-workers to search for new materials and mechanisms to convert triplets to singlet excited states. On excitation, the linear complexes ( $[\text{M}\{\{\text{amino}\}\text{(alkyl)carbene}\}\text{NR}_2]$  ( $\text{M} = \text{Cu}^I, \text{Au}^I$ )) studied undergo charge transfer from the amido (carbazolido, for example) to the carbene ligand and relax through photoluminescence. Certain  $\text{Cu}^I$  and  $\text{Au}^I$  complexes had a striking glow, initially assigned to phosphorescent or thermal emission, in line with the common wisdom described above. “We now think something far more interesting is going on,” explains Credgington.

How can emission from a  $T_1$  state occur in under  $1 \mu\text{s}$ ? One possibility is that the  $S_1$  and  $T_1$  states are sufficiently close in energy such that ISC is facile, as was revealed for the  $\text{Cu}^I$  and  $\text{Au}^I$  complexes using time-resolved spectroscopy. Monitoring the dynamics on timescales from

femtoseconds to milliseconds, Credgington’s team noted that the carbene and amido ligands — the ‘blades’ of the linear ‘propeller’ complex — rotate such that the dihedral angles between their planes vary from close to  $0^\circ$  in the virtually planar  $S_0$  and  $T_1$  states, to almost  $90^\circ$  in the rotated  $S_1$  state. When the ligands are co-planar, the  $T_1$  state is lower in energy than the productive  $S_1$  state, an order that is reversed when the ligand planes are perpendicular. In between lies a geometry — readily accessible owing to free rotation — at which the  $S_1$  and  $T_1$  states are degenerate and ISC is rapid. A single delayed-emission channel is responsible for the glow; one cannot distinguish whether excitation first affords the  $S_1$  state or the  $T_1$  state that must rotate to cross to  $S_1$ . However, regardless of the initial spin of the complex on excitation, it contributes to luminescence such that efficiency can approach 100%.

The thermal stability and photostability of the complexes are boosted by the weakness of their intermolecular interactions, which also enables solution processing for the fabrication of emissive films sandwiched between donor and acceptor layers — motifs that are useful in plastic electronics. The complexes emit green light, and the team aims to extend the design to emit near-IR (for medical diagnostics) as well as blue light (for RGB displays and white lighting). “Unlocking blue could have a huge impact on the display and lighting industries, finally making large-area, efficient OLED light sources a reality,” posits Credgington.

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**ORIGINAL ARTICLE** Di, D. et al. High-performance light-emitting diodes based on carbene-metal-amides. *Science* <http://dx.doi.org/10.1126/science.aah4345> (2017)