

Direct observation of intersystem crossing in a thermally activated delayed fluorescence copper complex in the solid state

Larissa Bergmann,^{1,2*} Gordon J. Hedley,^{3*} Thomas Baumann,² Stefan Bräse,^{1,4} Ifor D. W. Samuel^{3†}

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Intersystem crossing in thermally activated delayed fluorescence (TADF) materials is an important process that controls the rate at which singlet states convert to triplets; however, measuring this directly in TADF materials is difficult. TADF is a significant emerging technology that enables the harvesting of triplets as well as singlet excited states for emission in organic light emitting diodes. We have observed the picosecond time-resolved photoluminescence of a highly luminescent, neutral copper(I) complex in the solid state that shows TADF. The time constant of intersystem crossing is measured to be 27 ps. Subsequent overall reverse intersystem crossing is slow, leading to population equilibration and TADF with an average lifetime of 11.5 μ s. These first measurements of intersystem crossing in the solid state in this class of mononuclear copper(I) complexes give a better understanding of the excited-state processes and mechanisms that ensure efficient TADF.

INTRODUCTION

Organic light-emitting diodes (OLEDs) (1, 2) have shown remarkable progress from a laboratory-based technology to large-scale industrial mass production. Key challenges remain in establishing low-cost high-efficiency materials for the conversion of as much of the injected charge into light as possible. The most promising strategy is the use of thermally activated delayed fluorescence (TADF) (3, 4), whereby otherwise lost dark triplet excitons are back-converted into emissive singlets, with intersystem crossing (ISC) being the fundamental process that governs the conversion of singlets to triplets and vice versa.

Initial OLEDs used singlet excitons formed in fluorescent materials, giving an upper limit of 25% for device efficiency due to spin statistics. In so-called “second-generation” OLEDs, namely, those that use metal complexes such as iridium(III) compounds, strong spin-orbit coupling from the heavy metal is used to enable fast ISC and triplet emission (5–9). Such phosphorescent emitters enable 100% of generated excitons to be harvested for the emission of light but require the use of heavy metals. The concept of TADF has proven to be an alternative strategy for high efficiencies based on more abundant starting materials with small spin-orbit coupling, such as luminescent copper(I) complexes (3, 10–21) or carefully designed organic emitters (4, 22–26). These materials also enable 100% internal device efficiencies by using both singlet and triplet excitons.

Recently, various copper(I) complexes with different structural motifs, such as tetrahedral or trigonal coordinated mono-, di-, tri-, or tetranuclear copper(I) complexes, have been studied (3, 10–21). In these materials, the central copper(I) atom with a moderate spin-orbit coupling ($\xi_{\text{Cu}} = 857 \text{ cm}^{-1}$) (27) induces mixing of the excited singlet and triplet states and a small energy splitting between them, which leads to presumed fast intersystem crossing to the triplet and back. Repopulation of the excited singlet excitons at ambient temperature gives rise to thermally activated delayed fluorescence. This phenomenon was first proposed in the

early 1980s by McMillin (28) for copper(I) bis(phenanthroline) complexes and later used by several research groups to design highly efficient emitting materials based on the plentiful metal copper. The use of singlet states (3, 14) enables copper(I) complexes to emit fluorescence at shorter wavelengths (compared to phosphorescence) because the excited singlet is naturally higher in energy than the triplet and has a short emission decay time, which are crucial for the efficiency of an OLED at high currents.

Particular organic materials designed to have a narrowed energy gap between the excited singlet and triplet states have also been found to show TADF (4, 22–26). In all efficient TADF emitters, the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) are spatially separated on a donor and an acceptor part of the molecule, which leads to a small energy splitting between the excited singlet and triplet states (ΔE_{ST}) and thus faster ISC. The major difference of copper(I) complexes compared to all-organic molecules is higher spin-orbit coupling and thus intrinsically faster intersystem crossing. In addition to the generally faster emission decay times, the ease of emission color tunability by ligand variation makes copper(I) complexes an attractive alternative approach to organic emitters. A current challenge in the study of TADF systems is the unraveling of the various excited-state processes that occur, including radiative and nonradiative decay rates from the singlet, the rate of ISC, the rates of radiative and nonradiative losses in the triplet, and the rates of reverse intersystem crossing (RISC) from the triplet to singlet. Determining these rates can be challenging; thus, unambiguous observation of any of the key rates is valuable to the development of TADF materials. Knowing the rate of ISC enables the assessment of the suitability of materials as emitters in OLEDs, and as such is an important parameter in TADF systems.

This is the first known report on the intersystem crossing rate of a highly luminescent, TADF copper(I) complex in the solid state. This is crucial for the understanding of singlet utilization in OLEDs and the design of luminescent copper(I) complexes with short emission decay times. We chose a strongly emissive mononuclear TADF complex as a representative example of copper(I) complexes. We study the short-lived photoluminescence (PL) of the singlet metal-to-ligand and intraligand charge transfer (ML+IL CT) state by time-resolved emission and measure a time constant of 27 ps for ISC. The subsequent TADF is found to have an average lifetime of 11.5 μ s.

¹Institute of Organic Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany. ²CYNORA GmbH, Werner-von-Siemensstraße 2–6, Building 5110, 76646 Bruchsal, Germany. ³Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, Fife KY16 9SS, UK. ⁴Karlsruhe Institute of Technology (KIT), Institute of Toxicology and Genetics, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

*These authors contributed equally to this work.

†Corresponding author. E-mail: idws@st-andrews.ac.uk

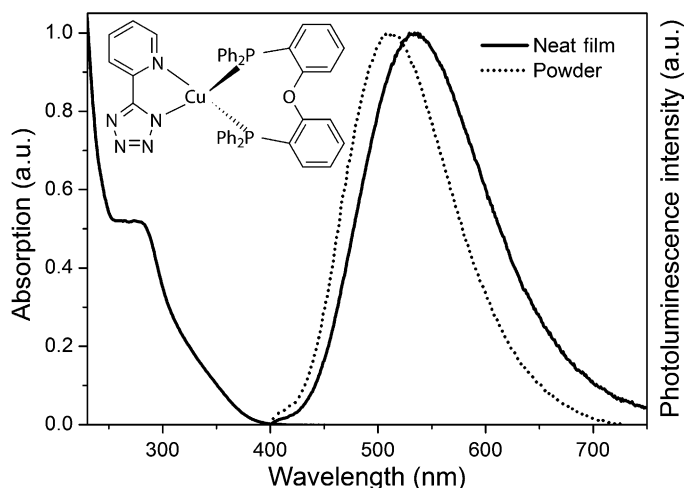


Fig. 1. Absorption and emission spectra of [(DPEPhos)Cu(PyrTet)] in neat film. The solid line represents neat film. The dashed line shows the emission spectrum of amorphous powder. a.u., arbitrary unit. The chemical structure of [(DPEPhos)Cu(PyrTet)] is shown in the inset.

RESULTS

We selected the compound [(bis(2-(diphenylphosphino)phenyl)ether)Cu(5-(2-pyridyl)tetrazolate)], denoted as [(DPEPhos)Cu(PyrTet)] (structure inset in Fig. 1), because this model compound represents an important class of neutral, mononuclear metal complexes that show TADF, assigned on the basis of a delayed component to the emission, the lifetime of which increases significantly when going to low temperatures along with a spectral shift indicative of change from singlet to triplet emission (11). It shows bright green emission with a peak at 535 nm and a PL quantum yield of 37% in neat film. The absorption and steady-state PL spectra of [(DPEPhos)Cu(PyrTet)] in amorphous powder and neat film are shown in Fig. 1.

As has been reported previously for this material in dichloromethane solution (11), the copper(I) complex exhibits strong absorption bands at 260 to 281 nm in film, which were assigned to ligand-centered transitions. Density functional theory (DFT) calculations predict a metal-to-ligand charge transfer (MLCT) transition with a strong intraligand charge transfer (ILCT) character localized on the anionic N⁻N ligand, which is confirmed by the very subtle ¹MLCT shoulder at 339 to 341 nm. The PL maximum at 512 nm in the amorphous powder is red-shifted to 535 nm in the neat film, which is due to different intermolecular interactions or molecular environments, which could possibly lead to slightly distorted molecule geometries in neat film compared to powder (29–31). The strong influence of the environment on the photophysical properties of copper(I) complexes is further reflected in the broad emission spectra of [(DPEPhos)Cu(PyrTet)] as a result of a distribution of slightly different conformations.

Time-resolved photoluminescence was initially measured on a microsecond time range, and the results are shown in Fig. 2, with the experimental methods described in Materials and Methods. Luminescence decay dynamics at the PL maximum of the steady state TADF luminescence show long-lived emission, fitting to a biexponential decay function by convolving with the instrument response function (IRF) and giving lifetime components (and pre-exponential factors) of 7.5 μs (0.57) and 16.8 μs (0.43), which may correspond to different coordination envi-

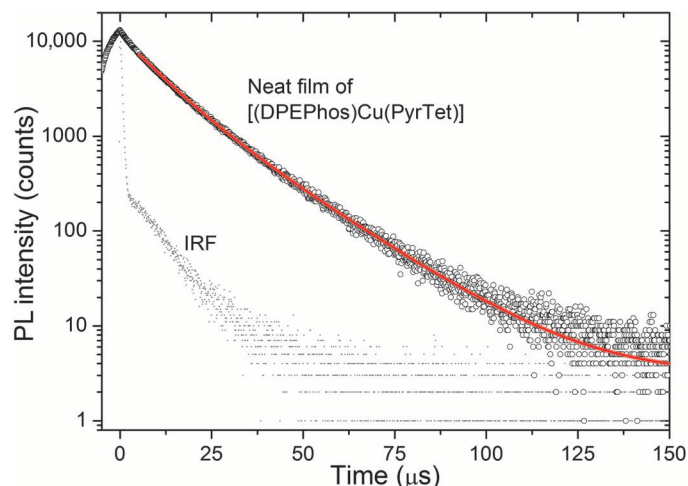


Fig. 2. Microsecond photoluminescence decay dynamics of [(DPEPhos)Cu(PyrTet)] in neat film following excitation at 378 nm, detected at 535 nm (PL maximum). The red solid line represents a fit to a biexponential decay with a time component of 7.5 μs (0.57 pre-exponential amplitude) and a component of 16.8 μs (0.43), which gives a weighted average lifetime of 11.5 μs. The IRF is also shown.

ronments in the film (31). A weighted average lifetime of 11.5 μs is determined by using the equation $\tau_{Ave} = \Sigma A_i \tau_i / \Sigma A_i$, with A_i as the pre-exponential factors for the lifetime. In this measurement, any fast (<1 ns) dynamics are not observed owing to the long temporal response of the time-correlated single photon counting method.

The picosecond luminescence decay dynamics of a neat film at a wavelength region 540 to 600 nm, which is around the PL maximum and on the red side of the PL, are shown in Fig. 3A, with the experimental details described in Materials and Methods. The observed decay can be fitted to a single exponential with a time constant of 27 ps when convolved with the IRF. This decay sits on a very strong background of long-lived emission lasting longer than 12 ns (the measurement frequency being 80 MHz), making the observation of the 27-ps decay challenging. Data acquisition over longer periods enabled the fast decay to become discernible from the background noise, with careful frequent sample position changes and monitoring of the background PL used to ensure that no sample degradation was occurring. To confirm that this decay does not embody a spectral shift within the singlet state, we recorded the time-resolved spectra as shown in Fig. 3B and found that in the time windows of 0 to 20 and 40 to 60 ps, the two PL spectra are essentially the same, and both agree with the PL spectrum for the long-lived (>12 ns) background from the measurement, which is representative of TADF emission. The long-lived spectrum was subtracted from both picosecond spectra to ensure that the background did not alter their shapes. Spectra without normalization that show the picosecond decay are provided in fig. S1A.

DISCUSSION

To understand the excited-state processes in the copper(I) complex [(DPEPhos)Cu(PyrTet)], we examined the photoluminescence on picosecond, nanosecond, and microsecond time scales to aid in our assignments. Figure 4 shows a schematic model of the photophysical processes in [(DPEPhos)Cu(PyrTet)].

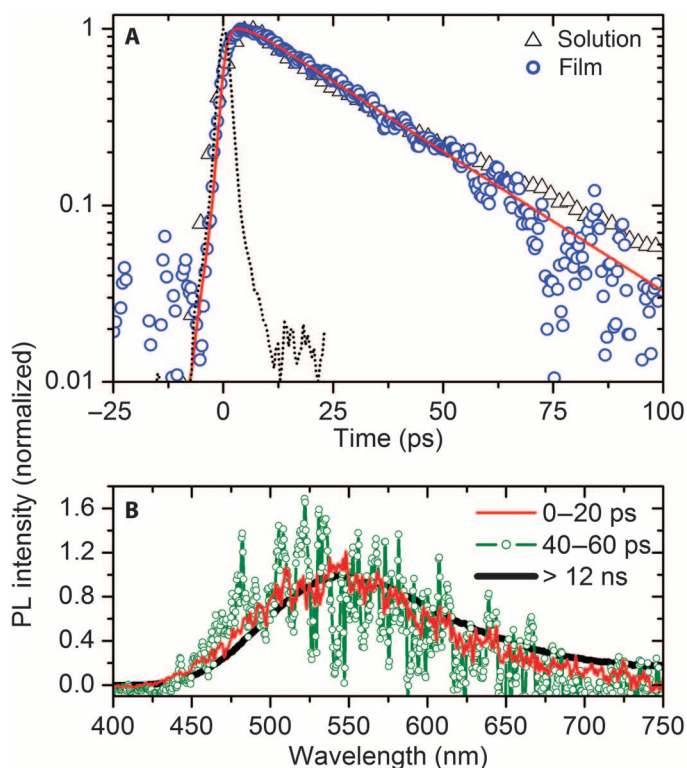


Fig. 3. Time-resolved photoluminescence of [(DPEPhos)Cu(PyrTet)] on the picosecond time scale. (A) Picosecond photoluminescence decay dynamics of [(DPEPhos)Cu(PyrTet)] in neat film (open circles) and dissolved in THF (open triangles) detected at 540 to 600 nm, representing emission from the PL maximum and red side. The solid line represents a fit to a monoexponential decay with a time constant of 27 ps. The IRF is depicted as a dotted line with 2.5 ps FWHM. (B) Normalized time-resolved PL spectra of the neat film in the time windows of 0 to 20 ps (red line) and 40 to 60 ps (green line with symbols) and long-lived PL for times longer than 12 ns (thick black line) derived from the background of the measurement.

Our primary interest lies in what happens in the initial phase after excitation of the system, that is, how quickly excitons relax to the lowest excited singlet S_1 state and then undergo ISC to the triplet state T_1 . From photoluminescence dynamics on the picosecond time scale (Fig. 3), a single fast decay of 27 ps is observed. We are left to interpret this decay with the knowledge that excitons in the triplet state do not emit much (or, more likely, any) light. Thus, when measuring the rapid decay of the PL in the wavelength region 540 to 600 nm, emission from the singlet state S_1 is observed. The main processes that can occur after photoexcitation are relaxation to the lowest excited states/lowest energetic sites due to environmental inhomogeneity (32, 33) and ISC to the triplet state. Time-resolved spectra in the time windows of 0 to 20 and 40 to 60 ps are essentially the same, indicating that this decay is not linked to any spectral relaxation or vibrational cooling in the singlet state, showing that these processes must be faster or slower than the time scale that we focus on here. Dissipation of excess energy in processes such as $S_2 \rightarrow S_1$ internal conversion was reported on a time scale of 50 to 100 fs for copper(I) bis(imine) complexes, whereas a subsequent flattening distortion is strongly correlated to the steric hindrance of the complex geometry and can reach subpicosecond time scales for complexes with bulky phenanthroline ligands (34–36) or can even be absent for sterical-

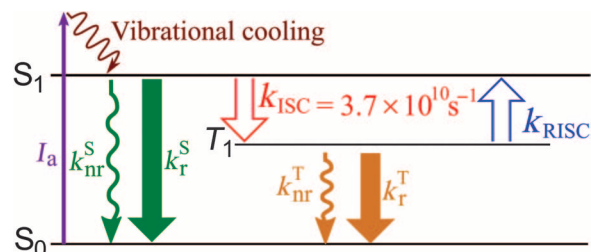


Fig. 4. Schematic representation of excited-state transitions in [(DPEPhos)Cu(PyrTet)]. Shown are r , radiative transition (solid arrows); nr , nonradiative transition (oscillatory arrows). After excitation to the excited singlet state (I_a), intersystem crossing to the triplet state occurs (k_{ISC}). At sufficient temperature, the excitons are repopulated to the excited singlet state (k_{RISC}), and subsequently thermally activated delayed fluorescence occurs. k_S and k_T depict the rate constants from the excited singlet or triplet state, respectively.

ly restricted molecules (37). However, substantial structural changes of the molecule [(DPEPhos)Cu(PyrTet)], such as the reported flattening distortion after excitation, apparently do not occur in the observed picosecond time window because this would result in a spectral red shift with time. To further confirm that exciton hopping to the lowest energy sites is not occurring on this time scale, we measured the complex in solution, and although the emission is weak, we find an almost identical decay time of 26 ps (Fig. 3A). The similar decay dynamics of [(DPEPhos)Cu(PyrTet)] observed for neat film and solution in the 100-ps time window indicate a similar coordination geometry around the copper(I) center in both film and solution due to an apparently restricted geometry, or only a marginal effect of the potentially distorted complex in solution on the ISC process (distortions in solid state are much more restricted). Because of the weak emission of the complex in solution, a detailed study of the photophysics would reveal differing processes at work. We speculate that molecular reorganization in the excited state leads to fast nonradiative decay. This is most likely from the triplet, owing to the very similar ISC time that is observed in solution and film. Indeed, the very similar times in solution and film tell us that the environment surrounding the complex [namely, tetrahydrofuran (THF) solvent molecules or other [(DPEPhos)Cu(PyrTet)] molecules] has little effect on the rate of ISC. Consequently, we assign the 27-ps process to ISC, consistent with the observation that, after this process, no further emission is observed on a time scale shorter than 12 ns (with the measurement frequency being 80 MHz); that is, all subsequent emission is delayed fluorescence. After the excitons have transferred to the triplet, reverse intersystem crossing back to the excited singlet occurs, giving TADF emission. The delayed component (Fig. 2) is reported as an average lifetime, consisting of two exponential decay components. The exact nature of these two components is out of the scope of this work but may well represent conformational disorder of the molecules in the film. What is important and interesting to note is that whereas conformational disorder may play a role in the dynamics of the delayed component, the process of interest here—ISC—is a single exponential decay of 27 ps, indicating that such disorder does not have an appreciable effect on the time constant of ISC. Reverse intersystem crossing is a subtle process that is difficult to observe. According to the Boltzmann statistics, very small proportions of the triplet state will return to the singlet at any given time, leading to a steady-state condition, with continual RISC to maintain the correct population ratios. Owing to the fast rate of intersystem crossing, RISC that does occur will have a high probability of being

delivered straight back to the triplet again, thus leading to a high degree of cycling between the singlet and triplet with slow loss of population via singlet radiative decay in high-efficiency materials such as the complex studied here. We thus can conclude that the time constant of 27 ps found for the luminescence decay dynamics from 540 to 600 nm can be attributed to intersystem crossing from $S_1 \rightarrow T_1$. This gives an ISC rate of $3.7 \times 10^{10} \text{ s}^{-1}$ ($= \tau_{\text{ISC}}^{-1}$).

We investigated broadband picosecond transient absorption dynamics for [(DPEPhos)Cu(PyrTet)] in neat film to attempt to observe the ISC process (fig. S2). Because of spectral overlap of strong long-lived photoluminescence (535 nm), the negative signal of excited-state absorption (ESA) was very noisy despite subtraction of the background fluorescence before analysis. This forbade detailed tracking of the temporal dynamics; however, we can see that that ESA decays on a similar time scale of tens of picoseconds to that observed with much better quality data in time-resolved PL. This result qualitatively complements the assignment of the observed kinetics to ISC; however, if similar singlet and triplet ESA bands exist, or they overlap strongly with the photoluminescence, then the crossing can be very challenging to measure, as was found here.

The small spin-orbit coupling constant of copper ($\xi_{\text{Cu}} = 857 \text{ cm}^{-1}$) is reflected in the rather slow ISC of 27 ps compared to iridium(III) complexes ($\xi_{\text{Ir}} = 3909 \text{ cm}^{-1}$) (27) with ISC time constants of ~ 100 fs (6, 7). Nevertheless, copper(I) complexes can harvest both triplet and singlet excitons for the emission of light and achieve internal quantum efficiencies of 100% (10, 30) by using the smaller spin-orbit coupling for thermally activated delayed fluorescence.

When compared to reported ISC constants of copper bis(imine) complexes that exhibit TADF in solution (10 to 15 ps) (35, 38–41), the time constant of 27 ps in the studied TADF [(DPEPhos)Cu(PyrTet)] in the solid state appears to be slower than one would expect. This indicates a weak effective spin-orbit coupling in the molecular orbitals involved in the emission, which is intrinsically controlled by ligands and/or halides coordinated to the copper(I) center and the specific coordination geometry (38). DFT calculations also confirmed an ML+IL CT transition with a small percentage of copper(I) interactions (weak internal heavy atom effect) (19). In addition to the intrinsic control of the ISC rate by ligands and/or halides, the environment and morphology can have a strong influence by changing the molecular ground- or excited-state geometry or by opening up other channels for ISC by the ease of structural changes, for example, in solution (38, 41). This shows the importance of solid-state measurements for the understanding of photophysical processes in an OLED because this replicates the state of matter that exists in working devices. The benefit of faster intersystem crossing when compared to all-organic emitters is that a greater tolerance is enabled on the energy splitting between singlet and triplet; thus, modifications can be made to the chemical structure for advantageous optoelectronic properties with less risk of switching off TADF.

The overall PL lifetime that we observe for TADF is comparable to other mononuclear neutral copper(I) complexes based on N[^]N and P[^]P ligands, which exhibit TADF lifetimes in the solid state in a similar range, that is, 13 to 54 μs (3, 20, 42, 43). By applying different ligand systems (44) or by using polynuclear copper(I) complexes and introducing halides (13–15, 45), the TADF lifetimes can be significantly reduced down to 2 to 4 μs while still maintaining high PL quantum yields, thus leading one to ask what the rate of ISC would be in those materials.

To conclude, the picosecond dynamics of a highly luminescent TADF copper(I) complex [(DPEPhos)Cu(PyrTet)] have been measured in the solid state by means of time-resolved photoluminescence and transient

absorption spectroscopy. In time-resolved photoluminescence measurements, we have observed a 27-ps decay representing intersystem crossing from the excited singlet state S_1 to the triplet state T_1 with a rate constant of $3.7 \times 10^{10} \text{ s}^{-1}$. This is the first time a direct observation of ISC in the solid state of a TADF copper complex has been reported, and contributes to the ability to understand the numerous excited-state processes by unambiguously measuring the rate of ISC. After the exciton has crossed to the triplet, reverse intersystem crossing back to the singlet occurs on a longer time scale by thermal activation, giving rise to an overall average PL lifetime of 11.5 μs . The copper(I) complex [(DPEPhos)Cu(PyrTet)] represents a promising class of emitter material for OLED applications. The determination of the ISC rate in such highly emissive compounds is challenging but very important for the understanding of the excited-state mechanisms in TADF materials that can be used in OLEDs. Implications of such fast intersystem crossing in a TADF OLED material include the realization of molecules that enable high device efficiencies without very demanding small singlet-triplet gap requirements; that is, fast ISC can be used to make up for a slightly larger gap while still enabling back-transfer from the triplet to singlet. For copper(I) complexes, future exploration of molecules with different structural motifs may offer the ability to (further) tune the ISC rate and, thus, the overall TADF efficiency and emission decay time to improve performance in OLEDs while also enabling adjustment of the emission color by ligand modifications.

MATERIALS AND METHODS

General information

The compound [(DPEPhos)Cu(PyrTet)] was synthesized according to literature methods (11). Solvents were purchased from VWR and Sigma-Aldrich at spectroscopic grade.

Sample preparation

[(DPEPhos)Cu(PyrTet)] was studied as neat films prepared by dissolving the material in CH_2Cl_2 at concentrations of 20 mg/ml for streak camera and transient absorption measurements, and at 10 mg/ml for steady-state PL and time-correlated single photon counting measurements and spin-coating the solutions to form a solid-state thin film. [(DPEPhos)Cu(PyrTet)] was dissolved in THF for solution measurements; different solvents were used for solution measurements and film deposition owing to the required concentrations for spinning films. Because films were measured under an active vacuum of 10^{-5} mbar, any residual solvent would be removed from the film and would not influence the observed PL dynamics.

Photophysical measurements

All photophysical measurements were performed at room temperature, unless noted otherwise. Ultraviolet (UV)-vis absorption spectra were measured on a Thermo Scientific Evolution 201 UV-vis spectrometer and a Varian Cary 300 double beam spectrophotometer. Absolute PL quantum yields were measured using the integrating sphere method (46) with a Hamamatsu Photonics C9920-02G system purged by nitrogen. Emission and excitation spectra were recorded on a Horiba Scientific FluoroMax-4 spectrofluorometer. Emission lifetimes were measured under nitrogen on the same system using the time-correlated single photon counting method. For this, a SpectraLED was used as the excitation source [$\lambda = 314 \text{ nm}$, pulse full width at half maximum (FWHM) = 493 ns].

Decay curves were analyzed with the software DAS-6 and DataStation provided by HORIBA Jobin Yvon. Streak camera measurements of neat films were taken at a range of wavelengths from 540 to 600 nm on a Hamamatsu synchroscan universal streak camera, measuring at 80 MHz, giving an instrument response of 2.5 ps (FWHM). Measurements were completed in vacuum at 10^{-5} mbar. The excitation source for streak camera measurements was at 375 nm, which was derived from the frequency-doubled output of the signal of a parametric amplifier with pulses at 20 kHz and 300 fs (FWHM), pumped by a Pharos regenerative amplifier from Light Conversion. Care was taken to keep peak excitation powers low to avoid exciton annihilation or degradation effects. Because prompt fluorescence in copper(I) complexes is very weak, the signals had to be averaged from several scans (no change was observed during integrations). Transient absorption studies were undertaken by the pump/probe technique with a Spectra Physics Hurricane regenerative amplifier, producing pulses of 100 fs at 5 kHz and 800 nm. The pump (400 nm) was obtained by frequency doubling the fundamental, whereas the probe was a white light continuum (420 to 760 nm) generated with 800-nm amplified light focused on calcium fluoride. Because dynamics >2 ps were of interest, the setup was not corrected for spectral chirp. Detection of the continuum probe was made with a silicon photodiode array from the company Entwicklungsbüro Stresing, with transient absorption measured by chopping the pump at 2.5 kHz. The measurements were carried out under an active vacuum of 10^{-5} mbar to minimize photodegradation.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/2/1/e1500889/DC1>

Fig. S1. Time-resolved PL spectra at different delay times in the neat film.

Fig. S2. Broadband transient absorption kinetics in the wavelength region 400 to 800 nm with delay times of 35 and 100 ps after the pump pulse (400 nm) with long-lived background subtraction.

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