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Bridging the Efficiency Gap: Fully Bridged Dinuclear Cu(I)-Complexes for Singlet Harvesting in High-Efficiency OLEDs

Daniel Volz, Ying Chen, Manuela Wallesch, Rui Liu, Charlotte Fléchon, Daniel M. Zink, Jana Friedrichs, Harald Flügge, Ralph Steininger, Jörg Göttlicher, Clemens Heske, Lothar Weinhardt, Stefan Bräse,* Franky So,* and Thomas Baumann*

In the last decade, the technology of organic light-emitting diodes (OLEDs) has developed far beyond being a lab curiosity and is now used in smartphones, tablet PCs, and even TVs. New strategies to use singlet as well as triplet excitons have been a key step for this progress. The triplet harvesting approach uses phosphorescent heavy-metal complexes such as $Ir(ppy)_3$ to convert singlet into triplet excitons and subsequently emit light via phosphorescence. Today, this is the most common pathway to achieve highly efficient OLEDs with internal quantum efficiencies

Dr. D. Volz, Dr. C. Fléchon, Dr. D. M. Zink,
Dr. J. Friedrichs, Dr. H. Flügge, Dr. T. Baumann
cynora GmbH
Werner-von-Siemensstraße 2-6
building 5110, 76646 Bruchsal, Germany
E-mail: baumann@cynora.com
Dr. Y. Cheng, Dr. R. Liu, Prof. F. So
Department of Materials Science and Engineering
University of Florida
Gainesville, FL 32611-6400, USA
E-mail: fso@mse.ufl.edu
M. Wallesch, Prof. S. Bräse
Institute of Toxicology and Genetics
Hermann-von-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany
E-mail: braese@kit.edu
M. Wallesch, Prof. S. Bräse
Institute of Organic Chemistry
Karlsruhe Institute of Technology
Kaiserstraße 12, 76131 Karlsruhe, Germany
Dr. R. Steininger, Dr. J. Göttlicher, Prof. C. Heske, Dr. L. Weinhardt
ANKA Synchrotron Radiation Facility
Karlsruhe Institute of Technology
Hermann-v.-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany
Prof. C. Heske, Dr. L. Weinhardt
Institute for Photon Science and Synchrotron Radiation (IPS)
Karlsruhe Institute of Technology (KIT)
Hermann-v.-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany
Prof. C. Heske, Dr. L. Weinhardt
Department of Chemistry
University of Nevada
Las Vegas (UNLV)
4505 Maryland Pkwy, Las Vegas, NV 89154-4003, USA
Prof. C. Heske, Dr. L. Weinhardt
Institute for Chemical Technology and Polymer Chemistry (ITCP)
Karlsruhe Institute of Technology
Engesserstraße 18/20, 76128 Karlsruhe, Germany

close to unity.[1] However, the limit has not yet been reached with displays: Using OLEDs for lighting, smart-packaging, and other mass-market applications has remained a dream since the first working OLED-devices were demonstrated in the late 1980s.[2] The realization of this long-term goal is hindered by the very low abundance of iridium in the earth's crust (0.0003 ppm[3] and the tendency of phosphorescent iridium emitters to self-quench, especially when using low-cost wet chemical production processes. This is often caused by aggregation and subsequent triplet–triplet annihilation by the phosphorescent emitter molecules themselves.[4] A recently established, alternative approach to achieve highly efficient OLEDs is to use thermally activated delayed fluorescence (TADF) materials as the emitter.[5] In contrast to triplet harvesting, TADF materials for singlet harvesting require a small singlet–triplet splitting $\Delta E(S_1–T_1)$, being in the order of the thermal energy $k_B T$, to enable a dynamic equilibrium between the singlet and triplet excited states. Both singlet and triplet excitons may be harvested for emission from the S_1-state by delayed fluorescence, a process which usually exhibits an emission decay time τ of several μs – a decay time similar to state-of-the-art phosphorescent emitters (**Figure 1**). Adachi and co-workers have demonstrated the feasibility of this approach by using specifically designed organic molecules without metals, which were processed by vacuum-deposition techniques and reached an external quantum efficiency (EQE) of 20% and more.[6–8] In order to minimize $\Delta E(S_1–T_1)$, the exchange integral between S_1 and T_1 and thus the spatial overlap of the frontier orbitals HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) has to be reduced.[9] This criterion is easily satisfied by using charge-transfer emitters.

In addition to the recent work on organic singlet harvesting emitters,[6–8] Cu(I)-complexes have been used for the same purpose. Copper is more than five orders of magnitude more abundant than iridium (68 ppm in the earth's crust[3] and common synthetic procedures for Cu(I)-complexes are characterized by a fast and often high-yield conversion of commercially available ligands.[10] In fact, the performance of the first OLEDs with Cu(I) emitters (in 1999) was similar to those with the first phosphorescent Ir(III) emitters.[11] Despite the benefits of Cu as a central metal in an emitter molecule, most studies focused on iridium and platinum, because high efficiencies could be achieved more easily. There are two reasons for this: (i) many Cu(I)-complexes are not suitable for vacuum-deposition, which was – at least back in 1999 – necessary to manufacture high-efficiency OLEDs and (ii) the specific photophysical
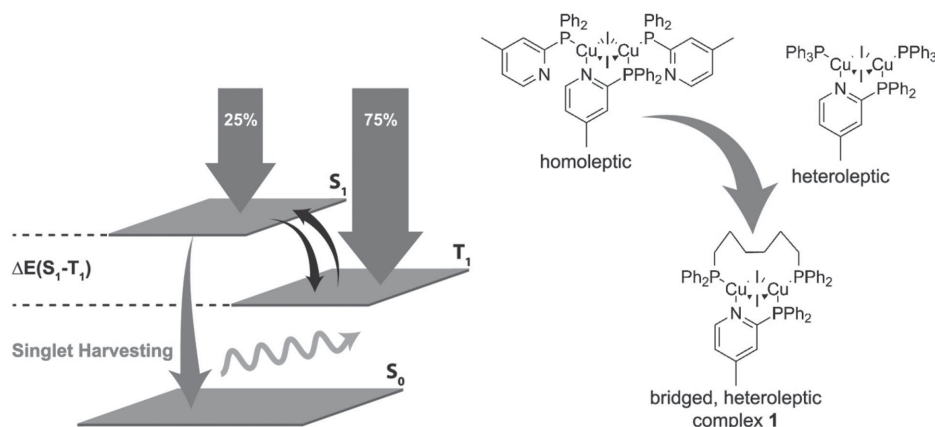
Figure 1. Left: A small singlet-triplet splitting enables a pseudo-equilibrium between S_1 and T_1. Emission occurs via delayed fluorescence from the S_1-state, harvesting both singlet and triplet excitons in an OLED. Right: Evolution of NHetPHOS-Cu(I)-complexes (arrow). The original homoleptic structure is modified by using different monodentate ligands to form heteroleptic complexes. Fusion of these ligands leads to a fully bridged, heteroleptic complex **1**.

benefits and demands of Cu(I)-complexes, namely the singlet harvesting mechanism, were not yet recognized. However, the singlet harvesting mechanism also comes with a side-effect that has to be addressed: if $\Delta E(S_1–T_1)$ is small, then the triplet energy $\Delta E(T_1–S_0)$ is rather high, unlike in phosphorescent organic molecules. Indeed, it has been pointed out that many Cu-complexes have very high triplet energies $\Delta E(T_1–S_0)$, which causes triplet excitons to leak into charge transport layers and therefore reduce the EQE.[12] The high triplet energy $\Delta E(T_1–S_0)$ has to be addressed in an appropriate way, e.g., by choosing matching charge-transport materials with an equally high triplet energy. Research also focused on mononuclear emitters of the type $[Cu(N,N)(P,P)]^+$, with (N,N) = phenanthroline-derivative and (P,P) = bisphosphine, but failed in realizing efficient devices.[13–15] In the meantime, it was shown that such Cu(I)-complexes are prone to severe structural distortion in the excited state,[16,17] sensitive towards matrix rigidity,[18] and may also dissociate into homoleptic complexes $[Cu(P,P)_2]^+$ and $[Cu(N,N)_2]^+$.[19] The latter absorbs in the visible part of the electromagnetic spectrum[20] and is thus a potent quencher. In contrast, Deaton and co-workers used a multinuclear Cu(I)-emitter $[Cu_2(P,N,P)_2]$ in a vacuum-processed OLED, showed that this complex is a singlet harvesting emitter, and achieved an EQE of 16.1%.[21] However, the emitter used in that study has a photoluminescence quantum efficiency (PLQY ϕ) of less than 60% and is air-sensitive, which limits the maximum EQE and may hamper the industrial applicability of this particular compound.

In order to resolve the shortcomings of current Cu(I) emitters, we have recently established the NHetPHOS-system.[10] This class of Cu(I)-complexes consists of a butterfly-shaped Cu_2I_2 unit, which is bridged by an N,P-ligand and further coordinated by two ancillary phosphine ligands (Figure 1). NHetPHOS-complexes are air-stable and – as will be demonstrated below – have triplet energies $\Delta E(T_1–S_0)$ that are up to 200 meV lower than those reported for comparable green-emitting Cu-complexes.[10] It is beneficial to use multinuclear Cu-halide-complexes instead of mononuclear complexes because of the metal halide-to-ligand charge transfer ((M+X)LCT) character

of the emissive transition: Upon excitation, electron density is moved from the metal-centered HOMO orbital to the ligand-centered LUMO orbital, which corresponds to a formal oxidation.[22] For mononuclear Cu(I)-complexes, the photoexcited species has profound Cu(II)-character, which leads to a flattening distortion (pseudo-planar geometry) in the excited state and subsequent quenching. When multinuclear complexes are used instead, the charge is delocalized and the entire Cu_2X_2 unit is oxidized. According to density functional theory (DFT) calculations, this leads to a smaller distortion in the excited state[22] and consequently helps to achieve high quantum efficiencies.

We thus developed a dinuclear, fully bridged NHetPHOS-complex (complex **1**) that shows a high thermal stability (T_{decomp} = 290 °C according to thermogravimetric analysis, TGA).[23] When doping thin films of a host material (e.g., PYD2) with **1**, a very high PLQY (close to unity) is noted comparable to homoleptic and nonbridged heteroleptic complexes. This may be the result of a reduced distortion upon excitation in thin-film morphology, an effect that has recently been found in nonbridged complexes.[23] Compared to the early examples of NHetPHOS-complexes, **1** exhibits improved film formation properties and a reduced crystallization tendency, even when prepared as neat thin films, i.e., without a host.

To gain insights into the atomic and electronic structure of the complex, we will first refer to X-ray and DFT results and then discuss the photophysical properties of thin films of **1**. Subsequently, the properties of a first optimized OLED device will be described. This device marks two important milestones: first, we close the performance gap to triplet harvesting iridium emitters by demonstrating that very high efficiencies can also be realized using Cu emitters. Second, we report (to the best of our knowledge) a new quantum efficiency record for both solution- and vacuum-processed OLEDs with Cu-complexes as emitters.

As mentioned in the introduction, the structural integrity of the molecule is of significant importance for its optoelectronic properties.[23] However, the commonly employed structure-determination method (single crystal X-ray diffraction) cannot
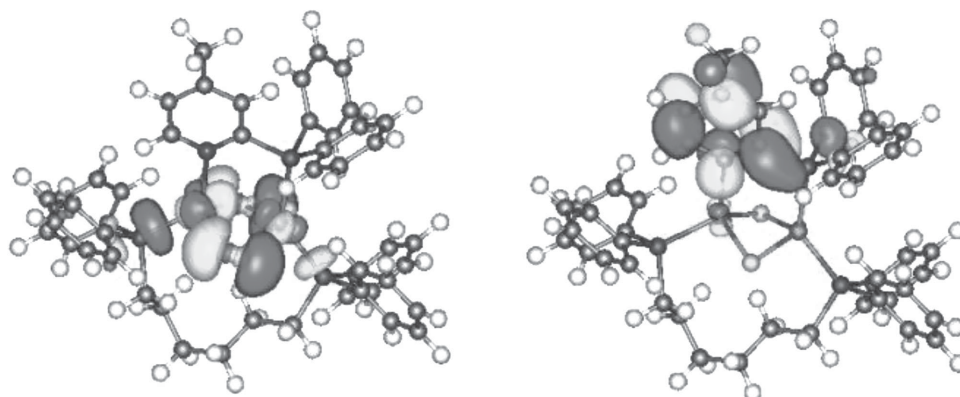
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Figure 2. HOMO (left) and LUMO (right) of complex **1** from DFT calculations with the BP86 functional.

be applied due to the low crystallization tendency of **1** and the lack of suitable single crystals. Instead, we employed X-ray absorption spectroscopy (XAS), which is a suitable method for structural analysis of amorphous samples.[24] XAS measurements at the Cu K edge in the X-ray absorption near-edge structure and extended X-ray absorption fine structure region indicated that the oxidation state of the Cu ions in complex **1** is +1, the coordination geometry around the Cu ions is similar to the distorted tetrahedral geometry in the homoleptic and heteroleptic complexes, and distances and coordination numbers of the nearest neighbors of the Cu(I) ion are in good agreement with the expected values for a NHetPHOS-complex (see the Supporting Information for details). Therefore, complex **1** shows the same coordination geometry with the same number and type of ligands as other NHetPHOS-complexes. These findings are important for the application of **1** in OLED devices, as the atomic structure of the emitter has to be controlled in order to allow for reproducible results and further optimization of the device.

To get a deeper understanding of its electronic properties, complex **1** was investigated from a quantum-chemical point of view. Theoretical and photophysical investigations provide valuable information for considering a particular OLED device architecture, e.g., concerning the HOMO and LUMO energies and their separation. These are important material properties that have to be considered for a particular OLED device architecture. The structures of complex **1** were optimized at the BP86/def2-SV(P) level in the ground state and in the lowest triplet state. The nature of the frontier orbitals (**Figure 2**) is comparable to the already known heteroleptic and homoleptic NHetPHOS complexes:[22,25] the HOMO is localized mainly on the Cu_2I_2 core, while the LUMO is mostly found on the bridging ligand. This suggests a (M+X)LCT-character of the lowest excitation, a fact that is further supported by time-dependent DFT (TD–DFT) calculations.

The vertical ionization energy of complex **1** is calculated to be 5.6 eV, which is in good agreement with a "photoelectron spectroscopy in air" measurement (5.3 ± 0.1 eV, see the Supporting Information). Based on the structures optimized using the BP86 functional, we performed TD–DFT calculations using the CAM-B3LYP functional. This functional is long-range-corrected and thus well suited to describe charge-transfer excited states. We used the ground-state geometry to calculate the

excitation and the triplet state geometry to derive the emission energies. The triplet excitation energy at the triplet geometry amounts to 2.55 eV and is identical to the experimental value of 2.55 ± 0.03 eV, which was determined as the onset of the emission spectrum at 77 K (as proposed recently,[12] see the Supporting Information). Comparable Cu(I) emitters often have triplet energies of 2.8 eV and more,[12] making it harder to confine triplet excitons to the emission layer (EML) in OLED devices. The calculated energy gap between the first excited singlet state and the lowest triplet state $\Delta E(S_1–T_1)$ is 0.09 eV (experimental value: 0.09 ± 0.04 eV, see the Supporting Information), i.e., ≈3.6 k_BT. In combination with the higher emission decay time at low temperatures and the red shift upon cooling (see below), this is commensurate with the idea that complex **1** shows TADF: The singlet harvesting mechanism was first found for a complex with $\Delta E(S_1–T_1) = 0.16$ eV,[5] which corresponds to 6.4 k_BT.

The emission and excitation spectra at room temperature and 77 K are given in **Figure 3**. Details regarding the PLQY and the excitation spectra are described in the Supporting Information. Several host materials were tested (see the Supporting Information). We point out that very high PLQY values up to
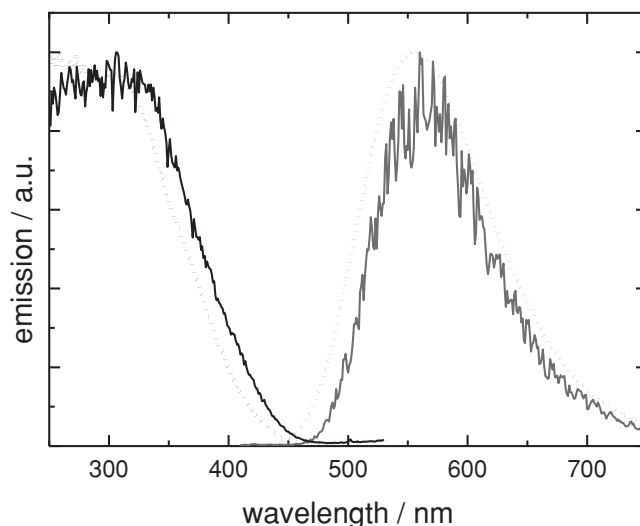

Figure 3. Emission (right) and excitation (left) spectra of complex **1** at room temperature (dotted lines) and at 77 K (solid lines).

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Φ = 92% ± 5% were measured in PYD2-doped films, while the emission decay time of 3.6 μs is considerably shorter than that for certain comparable green-emitting mononuclear compounds (31 μs in PYD2 films at room temperature).[12] This should enable an improved efficiency and reduced roll-off in an optimized OLED device. We hence focused on PYD2 for stack optimization.

Complex **1** promises to be an excellent emitter in a Cu(I)-based OLED device due to its good processability, the well-defined structure, low triplet energy, and high PLQY in PYD2-doped films, which is a result of the singlet harvesting mechanism. Therefore, solution-processed multilayer OLEDs with complex **1** were fabricated. To create a suitable OLED architecture for this emitter, we first estimated the energies of the frontier orbitals. As mentioned above, the HOMO energy at the surface of a drop-casted film was estimated to be 5.3 ± 0.1 eV below the vacuum level, and by subtracting the optical band gap of 2.7 ± 0.2 eV (see the Supporting Information), the LUMO energy at the surface is estimated to be 2.6 ± 0.3 eV below the vacuum level. With these estimates in mind, suitable materials (Figure 4, right) were selected to serve as blocking, transport, and contact layers in the OLED device (Figure 4, left).

We used indium tin oxide (ITO) coated glass substrates and poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate, or PEDOT:PSS, for the anode. Due to its compatibility with solution processing techniques and good hole transport properties, the thermally crosslinkable hole transport material PLEXCORE U314[26–28] was used for the hole transport layer (HTL). After the crosslinking process, the EML was processed from solution without blending or damaging the HTL. Tris[3-(3-pyridyl) mesityl]borane (3TPYMB) was used as the exciton blocking and electron transport layer (ETL) due to its high triplet energy and electron mobility.[29] This reduces loss processes of triplet excitons by triplet diffusion.[12] The complete device configuration is depicted in **Figure 4**, left: A 30 nm layer of PEDOT:PSS was spin-coated on the ITO substrate, followed by 45 nm of PLEXCORE UT-314, which was spin-coated and crosslinked as described in a recent publication.[28] The EML, consisting of complex **1** doped in PYD2 (27 nm) was then spin-coated on top of the HTL and dried on a hot plate. A 50 nm film of 3TPYMB

ETL was deposited by thermal evaporation, followed by 2 nm LiF and an Al cathode of 100 nm thickness.

Best results were achieved when annealing the EML at 80 °C for 5 min. Higher annealing temperatures or longer annealing times led to a decrease in device efficiency. Thermoanalytics were performed to rule out any degradation processes. No thermal degradation was observed for temperatures up to 290 °C (derived from TGA), and neither endothermic nor exothermic processes were found when heating complex **1** up to 200 °C (as monitored by differential scanning calorimetry).

This suggests that morphological changes in the EML are responsible for the impact of the annealing procedure (we were recently able to show how morphology effects may drastically influence the PLQY of NHetPHOS-complexes in powder samples).[22] We speculate that the impact of film preparation parameters on device efficiency is due to a similar effect.

The optimized "emitter : host" doping ratio for the complex **1**-based EML was found to be 3:7, while the optimized thickness was determined to be 27 nm (spin rate: 4000 rpm). The turn-on voltage of the resulting OLED device was found at 2.6 ± 0.1 V, while a maximum brightness of 10.000 ± 1000 cd m^{-2} was achieved at 10 V. Figure 7 shows the current efficiency as a function of luminance of the optimized device (top), together with its current density and luminance as a function of voltage (bottom). The current efficiency is 71 ± 2 cd A^{-1} at 100 cd m^{-2} and 47 ± 2 cd A^{-1} at 1000 cd m^{-2}. The peak current efficiency is 73 ± 2 cd A^{-1} at ≈40 cd m^{-2}, corresponding to a peak EQE of 23% ± 1%.

To the best of our knowledge, this is the highest EQE value ever reported for OLEDs with solution-processed EML based on Cu(I) emitters and is comparable to the efficiency of state-of-the-art thermally evaporated devices with Ir(III) emitters. The luminous efficacy of the OLED device presented here is significantly higher than those of current solution-processed record devices with green Cu emitters (49.5 cd A^{-1}).[12] and even the best vacuum-processed OLEDs with Cu emitters (65.3 cd A^{-1}).[30]

We note that the EQE of an OLED may be calculated by using the following, simplified equation:[5] EQE = $\chi_{out} \times \Phi_{PL} \times \beta \times \gamma$, with internal quantum efficiency (IQE) = $\Phi_{PL} \times \beta \times \gamma$ where χ_{out} = optical outcoupling factor, Φ_{PL} = PLQY of the EML

| 100 nm Al |
| 2 nm LiF |
| 50 nm 3TPYMB |
| 27 nm complex 1/PYD2 = 30/70 |
| 45 nm PLEXCORE UT-314 |
| 30 nm PEDOT:PSS |
| 130 nm ITO |

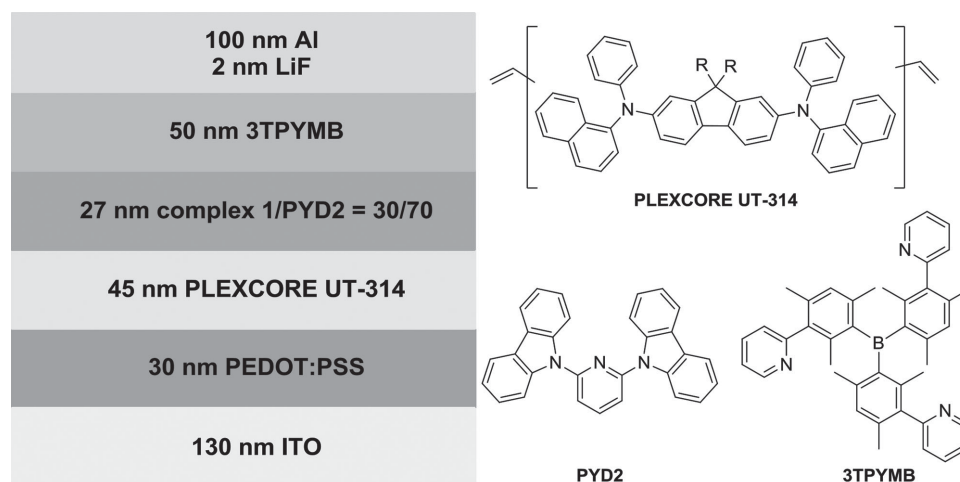PLEXCORE UT-314

PYD2

3TPYMB

Figure 4. Device architecture and molecular structures of the organic materials used herein.
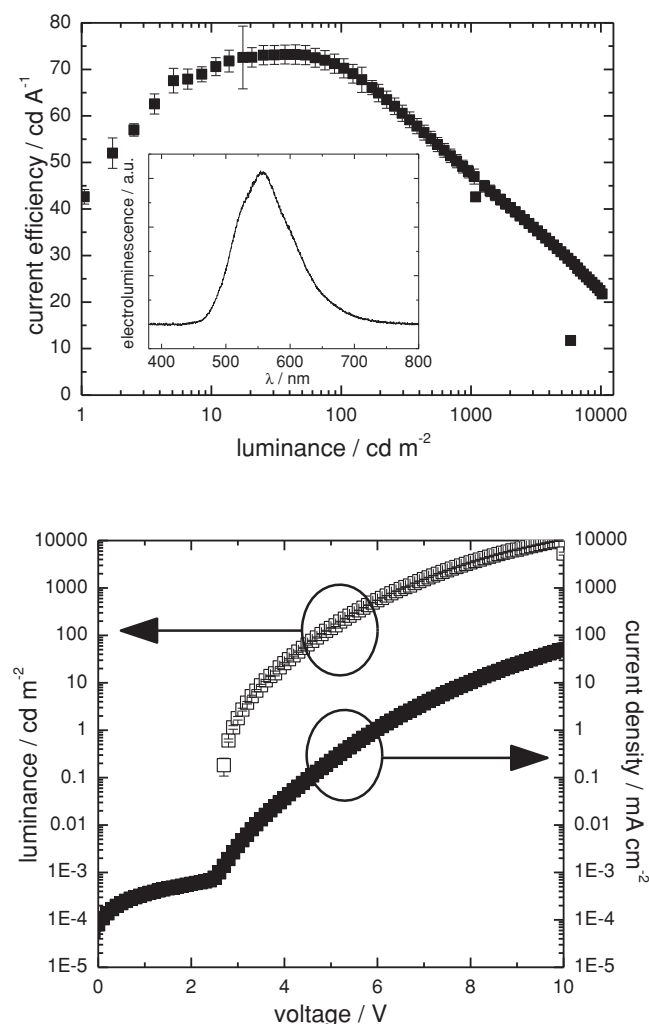
Figure 5. Top: Current efficiency versus luminance; inset: electroluminescence spectrum of the device. Bottom: Luminance (left ordinate) and current density (right ordinate) versus bias voltage. Error bars were determined based on intrabatch variations from different pixels.

value being 92%, close to unity. This finding is corroborated by estimating the IQE using the above-discussed assumptions for β, which yields an IQE identical to the PLQY, 92 ($\pm$5)%, as derived above.

Measurement and optimization of device lifetime was not within the scope of this study. So far, the highest lifetime ever reported for a Cu emitter is 440 h at 100 cd m^{-2} for a nonoptimized vacuum processed device[24] by Thompson and coworkers. Optimizing the lifetime of solution-processed devices is considerably more time consuming than for vacuum processes because variation of charge transport layers requires the development of crosslinkable materials and careful control of layer morphology. A common strategy is to use vacuum-processable model emitters and realize the resulting, optimized stack with crosslinkable analogues.[27] This way, the few issues we encountered can be solved: Figure 5 shows a decreasing efficiency at high luminance, a phenomenon commonly described as "efficiency roll-off."[4] While roll-off is often encountered in nonoptimized OLEDs, we note that the roll-off in this device is more pronounced than in highly optimized evaporated phosphorescent OLEDs. It has been reported that the loss of charge balance at high injection could be responsible for the severe efficiency roll-off in some phosphorescent OLEDs.[4] In fact, the sharp increase in the efficiency of our device at low luminance is a typical sign of a lack of charge balance at low injection conditions. Thus, further efforts are needed to understand and improve the charge balance and reduce the efficiency roll-off.

Due to the absence of concentration quenching in photoluminescence experiments, the very high PLQY (close to 100%) even in neat powders or crystals,[10] we speculate triplet–triplet annihilation to be weak for complex **1**. To prove this assumption would require PL experiments at high excitation intensity to simulate the concentration of excited molecules found at high current flow in an OLED. This work is currently in progress in our lab.

We have produced and presented an OLED device that is significantly more efficient than current solution-processed record devices with green Cu emitters[12] and even surpasses the best known vacuum-processed OLEDs with Cu emitters.[30] Future improvements will primarily be directed towards the optimization of adjacent charge transport layers (rather than optimization of the actual emitter material), which should improve the charge carrier mobility and the related roll-off effects, and also allow for optimization of device lifetime.

After 15 years of development, solution-processed Cu emitters finally bridge the efficiency gap and attain a level that is comparable with today's best green phosphorescent OLEDs using iridium or platinum. In order to reach very high efficiencies with Cu emitters, their particular chemical properties have to be considered: Molecular distortion upon excitation has to be suppressed, preferably by using multinuclear complexes with stable structural motifs, e.g., by use of fully bridging and chelating ligands. Also, it has been shown that the photophysics of Cu emitters may be influenced by matrix effects such as morphology and rigidity. This necessitates a careful optimization of processing parameters. Finally, it is possible to tap into the full potential of singlet harvesting emitters by careful optimization of the energy differences between the S$_0$, S$_1$, and T$_1$ level to simultaneously minimize the triplet energy

(determined to be 92% $\pm$ 5%, see above), β fraction of excitons that may be harvested and γ = charge balance factor. χ_{out} accounts for loss processes due to wave-guiding and interaction with the metal electrode and may be modeled if the refractive indices of all layers are known. Assuming that the device is a Lambertian light source with randomly oriented emitters, and that the refractive indices are similar to other OLED materials (1.7–1.9), we used a common approximate value of χ_{out} = 0.25 $\pm$ 0.05.[5,6] For the singlet harvesting mechanism, both singlet and triplet excitons may be harvested, meaning that β equals unity. We note that the charge balance, e.g., the ratio between holes and electrons in the EML often depends on the current. One could speculate that the charge carriers are balanced in the peak region of the luminance-efficiency plot (**Figure 5**), therefore $\gamma \approx 1$.

To derive an estimate for the IQE, we used the highest experimental value for EQE (23%) and χ_{out} = 0.25 $\pm$ 0.05. If all aforementioned assumptions are valid, the internal quantum efficiency IQE lies between 77% and 100%, with the most likely

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as well as the singlet–triplet splitting. In the present case, this was achieved by stabilizing the molecular structure using only bridging ligands, which opens a new pathway towards high-efficiency OLEDs with abundant and cost-effective components.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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