Recent Advances in Metal-TADF Emitters and Their Application in Organic Light-Emitting Diodes

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In this contribution, recent advances in new classes of efficient metal-TADF complexes, especially those of Au(I), Au(III), and W(VI), and their application in OLEDs are reviewed. The high performance (EQE = 25%) and long device operational lifetime (LT95 = 5,280 h) achieved in an OLED with tetraradentate Au(III) TADF emitter reflect the competitiveness of this class of emitters for use in OLEDs with practical interest. The high EQE of 15.6% achieved in solution-processed OLED with W(VI) TADF emitter represents an alternative direction toward low-cost light-emitting materials. Finally, the design strategy of metal-TADF emitters and their next-stage development are discussed.

Keywords: TADF, gold, tungsten, palladium, silver, organic light-emitting diode

INTRODUCTION

Thermally activated delayed fluorescence (TADF) materials have become a promising class of photo-functional materials with potential practical applications most exemplified in the field of organic light-emitting diodes (OLEDs). The majority of TADF materials reported to date are organic compounds having donor and acceptor moieties that give rise to emissive charge transfer (CT) excited states upon light excitation. By carefully positioning the donor(s) and acceptor(s), a small singlet-triplet energy gap (ΔE(S₁-T₁)) can be achieved, thereby allowing efficient reverse intersystem crossing (RISC) to singlet excited state and TADF to occur at room temperature. While numerous classes of molecular organic TADF materials have been reported, the diversity of metal complexes exhibiting TADF property is very limited. In this article, we discuss the recent advances on metal complexes which display TADF and their application in OLEDs.

RECENT ADVANCES IN METAL-TADF COMPLEXES AND THEIR APPLICATION IN OLEDs

Metal-TADF Light-Emitting Complexes

The burgeoning development of emitters for OLEDs started from the fluorescent metal complex 8-hydroxyquinoline aluminum (Alq₃) (Tang and VanSlyke, 1987). Despite its high luminance, high electron mobility and stability, the efficiency of Alq₃-based OLED is limited by its fluorescence nature. Theoretically, the upper limit of internal quantum efficiency (IQE) of a fluorescent OLED is about 25% as only singlet spin states can emit light in fluorescent emitters. In this regard, phosphorescent metal complexes have been attracting much attention considering the 100% potential IQE in electro-phosphorescence (Baldo et al., 1998; Ma et al., 1998). Typical phosphorescent emitters are heavy metal complexes such as those of Ru(II), Ir(III), Os(II), and Pt(II) with emission lifetimes (τ) ranging 1–100 µs due to significant mixing...
between the metal and ligand frontier molecular orbitals and the efficient spin-orbit coupling induced by the heavy metal atom. Because of their high luminescence efficiency and high stability, phosphorescent Ir(III) complexes have been widely used as emitting dopants in OLED industry (Baldo et al., 1999). Nonetheless, the earth abundance of iridium is the lowest among the metal elements, leading to sustainability concern. An alternative approach to harvest triplet excitons at room temperature is via TADF (Yersin et al., 2011; Uoyama et al., 2012). The key process in TADF is up-conversion from the lowest triplet excited state (T\(_1\)) to the lowest singlet excited state (S\(_1\)) which is then followed by fluorescence from S\(_1\) to the singlet ground state (S\(_0\)). Therefore, a delicate trade-off between \(\Delta E(S_1-T_1)\) and oscillator strength of S\(_0\)-S\(_1\) transition is crucial to achieve TADF. Since the reports by Endo et al. (2009), Deaton et al. (2010), and also by Uoyama et al. (2012), a plethora of organic TADF molecules have been reported (Wong and Zysman-Colman, 2017; Yang et al., 2017) but examples of metal-TADF emitters are mostly limited to copper complexes (Czerwieniec et al., 2016; Leitl et al., 2016). Since Cu(I) complexes generally lack thermal and electrochemical stability, efforts have been directed to develop 2nd and 3rd row transition-metal-TADF emitters such as those of Pd(II), Ag(I), Au(I), and Au(III) to meet the stringent requirements of emitters for practical OLEDs (Li G. et al., 2019). Gratifyingly, high external quantum efficiencies (EQEs) of up to 27.5 and 25.0% have been achieved in OLEDs with Au(I) and Au(III) TADF emitters, respectively (Di et al., 2017; Zhou et al., 2020), reflecting Au-TADF emitters as an emerging new class of competitive, emissive dopant in OLED industry.

The first report on electroluminescence (EL) of Cu(I) complex appeared soon after the reports on OLEDs based on Pt(II) and Os(II) emitters (Ma et al., 1999a,b). A Cu(I) complex could exhibit phosphorescence or TADF depending on its \(\Delta E(S_1-T_1)\) (Leitl et al., 2014). TADF could take place when the \(\Delta E(S_1-T_1)\) is comparable to the thermal energy \(k_B T\) that enables a dynamic equilibrium between S\(_1\) and T\(_1\). Several high-performance OLEDs based on Cu(I) complexes have been reported (Zhang et al., 2012, 2016; Cheng et al., 2015; Osawa et al., 2015; Volz et al., 2015; So et al., 2017; Hamze et al., 2019; Shi et al., 2019). For instance, Bräse, So, Baumann and co-workers reported EQEs of up to 23% for yellow-emitting OLEDs with an NHetPHOS-Cu(I) complex (NHetPHOS refers to a ligand having N-heterocycle and phosphine) as the emitter (Volz et al., 2015). Thompson reported a class of two-coordinate Cu(I) carbene amide complexes exhibiting photoluminescent quantum yields (PLQYs) up to 1.0 with \(\tau\) ranging 1.4–2.8 \(\mu\)s. EQEs of OLEDs fabricated with these emitters reached 19.4% (Shi et al., 2019). Since the development of TADF Cu(I) complexes has been well-reviewed (Czerwieniec et al., 2016; Yersin et al., 2017; Liu et al., 2018; Li G. et al., 2019), we will focus in this contribution on recent advances of efficient TADF metal complexes other than Cu(I) complexes that have been applied as emitting dopants in OLEDs.

### Silver TADF Complexes and Their Application in OLEDs

Several examples of Ag(I) TADF emitters have been reported recently. Lu discovered bis-dibenzolophosphine bridged binuclear Ag(I) halide complexes exhibiting TADF with PLQYs up to 0.98 and lifetime of 2.5–3.0 \(\mu\)s (Chen et al., 2016). Yersin reported a series of Ag(I) complexes supported by 1,10-phenanthroline and bis(diphenylphosphine)-nido-carborane (e.g., Ag-1, Figure 1) with PLQYs up to 1.0 and \(\tau\) ranging 1.4–2.8 \(\mu\)s (Shafikov et al., 2017a,b). Replacing 1,10-phenanthroline with a bridging tetraphosphine ligand afforded a binuclear Ag(I) TADF complex Ag-2 with PLQY of 0.70 and \(\tau\) of 1.9 \(\mu\)s (Shafikov et al., 2018). A Ag(I) carbene amide complex also exhibits TADF with PLQY of 0.74 and \(\tau\) of 460 ns in degassed toluene. OLEDs fabricated with this emitter showed EQEs up to 13.7% (Romanov et al., 2018).

### Gold TADF Complexes and Their Application in OLEDs

Gold is an attractive candidate for developing OLED emitters attributable to the high thermal stability endowed by strong gold-ligand bonds and its relatively high abundance among other noble metals in Earth’s crust. Due to the electrophilicity/relatively high reduction potential of Au(III), Au(III) complexes often display ligand-centered emission having minute metal contribution. This results in small radiative decay rate constants \(k_r\) of \(10^2\)–\(10^3\) s\(^{-1}\) and hence long \(\tau\) (usually >10 \(\mu\)s), longer than those of typical Ir(III) and Pt(II) complexes by one or two orders of magnitude (Zhou et al., 2019). As long emission lifetimes would cause severe efficiency roll-off in OLEDs (Cheng et al., 2014), only a few of them could achieve decent EQE and low efficiency roll-off at the same time. Notably, the study on Au(I)-OLEDs was even rarer than those of Au(III)-OLEDs (Ma et al., 1999a,b,c). In this regard, the recent development of TADF gold complexes has made a remarkable turnaround. Linnolahiti, Bochmann, Credgington and co-workers reported a series of 2-coordinate carbene–Au(I)–amides (CMAs) that consist of a cyclic (alkyl)(amino)carbene (CAAC) connected via Au(I) to a carbazolate or diphenylamide (Di et al., 2017). Computations revealed that \(\Delta E(S_1-T_1)\) of CMA-1 remains small (<800 cm\(^{-1}\)) along the torsional coordinate, even at the conical paraposition which has fluorescence rate of the order 10\(^7\) s\(^{-1}\), thus leading to a fast equilibration of the S\(_1\) and T\(_1\) excited states and a large \(k_r\) of \(2.4 \times 10^6\) s\(^{-1}\), PLQY of 0.83 and short \(\tau\) of ~350 ns in neat film at 300 K (Föller and Marian, 2017; Conaghan et al., 2018). A maximum EQE of 26.3% was achieved in solution-processed OLEDs with CMA1 as the emitter and high EQE of 24.5% was maintained at a luminescence of 1,000 cd m\(^{-2}\). Nonetheless, there has been no report on the operational lifetimes of the aforementioned Au(I)/Cu(I)/Ag(I)-TADF OLEDs. In 2017, Che and co-workers identified TADF as the emission origin in several pincer Au(III) aryl emitters (To et al., 2017). The presence of diarylamo group on the monodentate aryl ligand, and its twisted geometry with respect to the cyclometalating ligand, results in TADF in Au-1 (Figure 1). Based on variable temperature–emission lifetime measurements and DFT calculations, a \(\Delta E(S_1-T_1)\) of 318 cm\(^{-1}\) was estimated for this complex. With short \(\tau\) of 0.72 \(\mu\)s and high PLQY of 0.84 in room temperature, solution-processed OLEDs with Au-1 showed EQE and luminance of up to 23.8% and 57,340 cd m\(^{-2}\), respectively. It is noted that both devices based on the Au(I) complex CMA1 and the Au(III) complex Au-1 were fabricated by solution-processed technique. In this regard,
studies on EL of these gold complexes in vacuum-deposited devices were undertaken to determine if they have potential application in practical OLEDs. High maximum EQEs of 26.9 and 23.4% were achieved in vacuum-deposited OLEDs with Au(I) complex CMA1 (Conaghan et al., 2018) and pincer Au(III) alkynyl complex Au-2 (Figure 1; Zhou et al., 2019), respectively. Despite the slightly lower efficiency, the device lifetime (LT95) of the latter has been measured to be ~500 h at an initial luminance of 100 cd m\(^{-2}\), which is at least comparable to that of pincer Au(III) complex bearing deprotonated carbazole as auxiliary ligand reported by Li L.-K. et al. (2019). The improved thermal stability of Au(III) alkynyl complexes compared to the aryl ones is attributed to the stronger Au(III)-C\(_{sp}\) bond in the alkynyl counterparts. Au(I) complexes with diphosphine ligand(s) have also been reported to display TADF (Osawa et al., 2018). The crystalline solid of Au(I) diphosphine iodide (Au-3) displayed yellow photoluminescence with PLQY of 0.92 and lifetime of 9.0 µs. Its emission shows a red-shift of 20 nm, a decrease in PLQY to 0.74 and an increase of lifetime to 77 µs, corresponding to a reduction in \(k_r\) from \(1.0 \times 10^5\) s\(^{-1}\) to \(9.6 \times 10^3\) s\(^{-1}\) upon cooling from 293 to 77 K. Au(I) bis-diphosphine complex Au-4 exhibits a high PLQY of 0.95 but with much shorter lifetime of 3.8 µs. The \(\Delta E(S_1-T_1)\) of Au-3 and Au-4 were estimated to be 870 and 620 cm\(^{-1}\), respectively.

**Tetradentate Metal-TADF Emitters and Their Application in OLEDs**

The aforementioned TADF Au(I) and Au(III) complexes were prepared by using two ligands. Since the stability of metal complexes could be increased by employing chelating ligands of higher denticity, the employment of tetradentate ligand with C-donor atom(s) is envisaged to improve the thermal
stability and to restrict excited-state structural distortion of the resultant complex as exemplified in tetradeutate Pt(II) and Pd(II) complexes (Vezzu et al., 2010; Cheng et al., 2013; Chow et al., 2016). Furthermore, it was suggested that an increase in the structural rigidity of emitters could suppress structural deformation upon S1-T1 transformation, which reduces AE(S1-T1) and leads to efficient TADF (Saigo et al., 2019). Therefore, the development of TADF Au(III) complexes supported by trianionic tetradentate ligands would be an appealing direction toward practical Au-OLEDs. A class of Au(III) complexes supported by N-bridged tetradentate ligand prepared by post-modification was reported by Wong et al. (2017). These complexes exhibit photoluminescence from triplet intraligand charge-transfer (ILCT) excited states with PLQY of up to 0.78 in thin films. Solution-processed OLEDs fabricated with these emitters showed EQE of up to 11.1%. Che and co-workers developed new strategies for synthesizing tetradeutate Au(III) complexes with O-bridged/spiro-arranged C=N=C=N=C ligand by microwave induced C-H activation (Zhong et al., 2020). By rationally varying the substituent(s) on the ligand, the emissive excited states of the Au(III) emitters are changed from triplet intraligand (3IL) excited states with $k_r$ of $\sim$10$^3$ s$^{-1}$ to TADF from ILCT excited states. These Au(III) TADF emitters show high thermal stability and PLQYs of up to 0.94 and $\tau$ down to 0.62 µs in degassed toluene. A vacuum-deposited OLED with Au-5 as the emissive dopant showed maximum EQE of 25% and the EQE value maintained at 22% at a luminance of 1,000 cd m$^{-2}$. Significantly, as listed in Table 1, at an initial luminance of 100 cd m$^{-2}$, this device showed a much longer lifetime LT$95$ of 5,280 h. This value is at least 10-fold longer than those recorded with pincer Au(III) emitters (Li L.-K. et al., 2019; Zhou et al., 2019). This result highlights the advantage of using tetradeutate ligand in the preparation of robust Au(III) TADF emitters for practical use. It also showcases tetradeutate Au(III) TADF complexes as competitive candidate in OLED industry.

Tetradeutate ligand has also been used in preparing stable, luminescent Pd(II) complexes. Li and co-workers reported a tetradeutate Pd(II) complex, PdN3N, which contains a C=N cyclometalating moiety composed of 2-pyridyl-carbazole, where the T1 is localized, and also a donor-acceptor moiety of carbazole-carbazoyl-pyridine (Figure 1, Zhu et al., 2015). PdN3N exhibited both phosphorescence and TADF at room temperature with PLQY of 0.72. A maximum EQE of 20.9% and operational lifetime LT$90$ of 170 h at an initial luminance of 1,697 cd m$^{-2}$ were achieved in the OLED with PdN3N. Nonetheless, the EQE of this device dropped to $\sim$7.0% at a luminance of 1,000 cd m$^{-2}$. Such severe efficiency roll-off is a result of the long $\tau$ of $>100$ µs for PdN3N, which limits the application of this kind of Pd(II) complexes in practical OLEDs. In addition, the color purity of the Pd-OLED is not good enough because of the wide EL spectrum resulting from dual emission from both phosphorescence and TADF.

### Table 1: Key performances of selected metal-TADF complexes.

| Complex | Fabrication method | EQE (%) | L$^2$ (cd m$^{-2}$) | CIE* ($x$, $y$) | Lifetime$^f$ (h) |
|---------|-------------------|---------|-------------------|----------------|-----------------|
| CMA1    | SP$^a$            | 26.3    | 44,700            | 0.26, 0.49     | n. a.           |
|         | VD$^b$            | 26.9    | 35,400            | 0.24, 0.42     | n. a.           |
| Au-1    | SP$^a$            | 23.8    | 33,740            | 0.27, 0.51     | n. a.           |
| Au-2    | VD$^b$            | 23.4    | 70,300            | 0.40, 0.55     | 500             |
| Au-5    | VD$^b$            | 25.0    | 22,700            | 0.43, 0.54     | 5,280           |
| PdN3N   | VD$^b$            | 20.9    | n. a.             | 0.30, 0.61     | 6,000$^e$       |
| Zn-1    | VD$^b$            | 19.6    | n. a.             | n. a.          | n. a.           |
| W-1     | SP$^a$            | 15.6    | 16,890            | 0.49, 0.49     | n. a.           |

$^a$Solution process; $^b$Vacuum deposition; $^c$Estimated from the original reference; $^d$Maximum luminance; $^e$CIE coordinates; $^f$LT$95$ at $L_r = 100$ cd m$^{-2}$.

Inexpensive Metal-TADF Complexes and Their Application in OLEDs

The low earth abundance of noble metals (e.g., iridium, platinum) has stimulated a great interest to invent new classes of luminescent materials based on inexpensive, earth-abundant metals (Bizzarrri et al., 2018; Wenger, 2018). Besides Cull complexes, more examples of inexpensive metal-TADF emitters have been reported. Adachi and co-workers synthesized TADF materials based on zinc, magnesium and lithium having ILCT transition (Sakai et al., 2015). Zn-1 (Figure 1) was the most efficient emitter among these complexes. The EQE of vacuum-deposited OLEDs based on Zn-1 was up to nearly 20%. By employing terphenyl having carboxyl and diphenylamine groups as linkers, Adachi, Kabe and co-workers constructed a zirconium-based metal-organic framework exhibiting green TADF with PLQY of 0.30 under vacuum (Mieno et al., 2018).

Tungsten is another appealing candidate for developing luminescent metal-based materials because of its large spin-orbit coupling constant (2,433 cm$^{-1}$) which facilitates intersystem crossing and significantly higher earth abundance than noble metals. Nonetheless, examples of air-stable tungsten complexes displaying strong photoluminescence are rare with the recent report on W(VI) cis-dioxo Schiff base and quinolinolate complexes by Yeung et al. (2017). One of these complexes exhibit PLQYs of up to 0.22 in thin film and was used as emitter to realize the first tungsten-OLED, though the maximum EQE achieved was only 4.79%. While the proof of principle has been demonstrated, the low PLQY and inferior performance data suggested that significant improvement in the photo-luminescent
properties of luminescent W(VI) complexes is needed if the latter are to be used for practical applications. With a view to designing W(VI) complexes with competitive luminescent properties for OLED application, it is conceived that installation of diarylaminogroup(s) on the Schiff base ligand may change the emission origin to TADF (To et al., 2017; Zhou et al., 2019), thereby boosting $k_r$ and improving PLQY. Che and co-workers described the first example of tungsten TADF emitter in 2019 (Chan et al., 2019). This study has demonstrated that the incorporation of diarylamino donor groups into the ligand scaffold changes the emissive excited state from phosphorescence ($k_\text{ph}$) as those of Au(III), W(VI), and Pd(II). In these complexes, in complexes that are composed of electrophilic metal ion, such the recent findings, metal-TADF emitters are generally realized $k_\text{TADF} = 4.79\%$).

**DISCUSSION**

The variety and design strategy of metal-TADF emitters remain considerably scarce despite the recent discoveries on Au(I), Au(III), Ag(I), and Pd(II) TADF emitters. Summarizing from the recent findings, metal-TADF emitters are generally realized in complexes that are composed of electrophilic metal ion, such as those of Au(III), W(VI), and Pd(II). In these complexes, the emission origin is changed from phosphorescence (3LC) to TADF by adding donor groups to generate LLCT/ILCT excited states. The originally small $k_r$ of these complexes allows an easy identification of whether TADF is operative because a 100-fold (or even more) increase in $k_r$ would be observed when TADF takes place, as exemplified in Au(III) and W(VI) TADF emitters. This finding is similar to that of organic compounds which are shown to show long-lived phosphorescence ($k_\text{ph} < 100 \text{ s}^{-1}$). By incorporating donor-acceptor pair, TADF can be observed and the $k_\text{ph}$ of organic compounds can be increased significantly. Accordingly, it may be a challenge to realize TADF in Pt(II) and Ir(III) complexes due to their large phosphorescent $k_\text{ph}$ which facilitates efficient radiative decay via triplet excited state. Another consideration is that as the $k_\text{TADF}$ of phosphorescent Pt(II) and Ir(III) are already large (10$^5$–10$^6$ s$^{-1}$), switching the emission origin to TADF may not lead to a drastic increase in $k_\text{TADF}$ and this renders the identification of whether TADF is occurring in these complexes highly challenging.

Compared to pure organic TADF emitters, $\tau$ of triplet excited states of metal-TADF complexes is much shorter, which could be advantageous for the operational stability of OLEDs based on metal-TADF emitters. Furthermore, with the use of rigid tetradeinate ligands, a drastic improvement in terms of efficiency and device stability could be realized as that observed for tetradeinate Au(III) TADF emitters. This finding calls for a more stringent ligand design for practical metal-TADF emitters in addition to pursuing high PLQY and short $\tau$.

Besides, the questionable practicability of Cu(I) complexes in OLEDs triggers the investigation on TADF emitters based on other inexpensive metals. Although TADF Zn(II) and W(VI) complexes have shown high PLQY and EL efficiency, the improvement of operational lifetime of devices based on these complexes remains a formidable challenge. The deployment of robust and rigid ligands that would induce the occurrence of TADF could be the key to increase the practical potential of emitters based on earth-abundant metals.

**AUTHOR CONTRIBUTIONS**

All authors contributed to the writing of the manuscript.

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**REFERENCES**

Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., and Forrest, S. R. (1999). Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Appl. Phys. Lett.*, 75, 4–6. doi: 10.1063/1.124258

Baldo, M. A., O’Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., et al. (1998). Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* 395, 151–154. doi: 10.1038/25954

Bizzarri, C., Spuling, E., Knoll, D. M., Volz, D., and Bräse, S. (2018). Sustainable metal complexes for organic light-emitting diodes (OLEDs). *Coord. Chem. Rev.* 373, 49–82. doi: 10.1016/j.ccr.2017.09.011

Chan, K.-T., Lam, T.-L., Yu, D., Du, L., Phillips, D. L., Kwong, C.-L., et al. (2019). Strongly luminescent tungsten emitters with emission quantum yields of up to 84%: TADF and high-efficiency molecular tungsten OLEDs. *Angew. Chem. Int. Ed.* 58, 14896–14900. doi: 10.1002/anie.201906698

Chen, J., Teng, T., Kang, L., Chan, X.-L., Wu, X.-Y., Yu, R., et al. (2016). Highly efficient thermally activated delayed fluorescence in dinuclear Ag(II) complexes with a bis-bidentate tetraphosphane bridging ligand. *Inorg. Chem.* 55, 9528–9536. doi: 10.1021/acs.inorgchem.6b00068

Cheng, G., Chan, K. T., To, W.-P., and Che, C.-M. (2014). Color tunable organic light-emitting devices with external quantum efficiency over 20% based on strongly luminescent gold(III) complexes having long-lived emissive excited states. *Adv. Mater.* 26, 2540–2546. doi: 10.1002/adma.201304263

Cheng, G., Chow, P.-K., Kui, S. C. F., Kwok, C.-C., and Che, C.-M. (2015). High-efficiency polymer light-emitting devices with robust phosphorescent platinum(II) emitters containing tetradentate diaionic O’N’C’N’ ligands. *Adv. Mater.* 25, 6765–6770. doi: 10.1002/adma.201302408

Cheng, G., So, G. K.-M., To, W.-P., Chen, Y., Kwok, C.-C., Ma, C., et al. (2015). Luminescent zinc(II) and copper(I) complexes for high-performance
solution-protonated monochromic and white light emitting organic diodes. *Chem. Sci.* 6, 4623–4633. doi: 10.1039/C4SC0421J

Chow, P.-K., Cheng, G., Tong, G. S. M., Ma, C., Kwok, W.-M., Ang, W.-H., et al. (2016). Highly luminescent palladium(II) complexes with sub-millisecond blue to green phosphorescent excited states. Photocalysis and highly efficient PSE-OLEDs. *Chem. Sci.* 7, 6083–6098. doi: 10.1039/C6SC0462H

Conaghan, P. J., Menke, S. M., Romanov, A. S., Jones, S. T. E., Pearson, A. J., Evans, E. W., et al. (2018). Efficient vacuum-processed light-emitting diodes based on carbene–metal–amides. *Adv. Mater.* 30, 1802285. doi: 10.1002/adma.201802285

Czerwieniec, R., Leitl, M. J., Homeier, H. H. H., and Yersin, H. (2016). Cu(I) complexes–thermally activated delayed fluorescence. Photophysical approach and material design. *Coord. Chem. Rev.* 325, 2–28. doi: 10.1016/j.ccr.2016.06.016

Deaton, J. C., Switalski, S. C., Kondakov, D. Y., Young, R. H., Pawlik, T. D., Giesen, D. J., et al. (2010). E-type delayed fluorescence of a phosphine-supported Cu(η-NAr)2 diamond core: harvesting singlet and triplet excitons in OLEDs. *J. Am. Chem. Soc.* 132, 9499–9508. doi: 10.1021/ja094575s

Di, D., Romanov, A. S., Yang, L., Richter, J. M., Rivett, J. P. H., Jones, S., et al. (2017). High-performance light-emitting diodes based on carbene–metal–amides. *Science*. 356, 159–163. doi: 10.1126/science.aah4345

Endo, A., Ogawara, M., Takahashi, A., Yokoyama, D., Kato, Y., and Adachi, C. (2009). Thermally activated delayed fluorescence from Sn4+-Porphyrin complexes and their application to organic light emitting diodes—A novel mechanism for electroluminescence. *Adv. Mater.* 21, 4802–4806. doi: 10.1002/adma.200802376

Föller, J., and Marian, C. M. (2017). Rotationally assisted spin-state inversion in carbene-metal-amides is an artifact. *J. Phys. Chem. Lett.* 8, 5643–5647. doi: 10.1021/acs.jpclett.7b02701

Hamze, R., Pelletier, J. L., Sylvinson, D., Jung, M., Cardenas, J., Haiges, R., et al. (2019). Eliminating nonradiative decay in Cu(I) emitters: >99% quantum efficiency and microsecond lifetime. *Science*. 363, 601–606. doi: 10.1126/science.aav2865

Leitl, M. J., Krylova, V. A., Djurovich, P. I., Thompson, M. E., and Yersin, H. (2014). Phosphorescence versus thermally activated delayed fluorescence. Controlling singlet-triplet splitting in brightly emitting and sublimable CuI complexes. *J. Am. Chem. Soc.* 136, 16032–16038. doi: 10.1021/ja508515z

Leitl, M. J., Zink, D. M., Schinabeck, A., Baumann, T., Volz, D., and Yersin, H. (2016). Copper(I) complexes for thermally activated delayed fluorescence materials. *Chem. Commun.* 51, 3181–3184. doi: 10.1039/c4cc09403d

Shafikov, M. Z., Suleymanova, A. F., Czerwieniec, R., and Yersin, H. (2017a). Design strategy for Ag(I)-based thermally activated delayed fluorescence reaching an efficiency breakthrough. *Chem. Mater.* 29, 1708–1715. doi: 10.1021/acs.chemmater.6b05175

Shafikov, M. Z., Suleymanova, A. F., Czerwieniec, R., and Yersin, H. (2017b). Thermally activated delayed fluorescence from two-coordinate Cu(I) complexes featuring nonconventional N-heterocyclic carbene. *J. Am. Chem. Soc.* 141, 3576–3588. doi: 10.1021/jacs.8b12397

Shafikov, M. Z., Suleymanova, A. F., Schinabeck, A., and Yersin, H. (2018). Dinuclear Ag(I) complex designed for highly efficient thermally activated delayed fluorescence. *J. Phys. Chem. Lett.* 9, 702–709. doi: 10.1021/acs.jpclett.7b03160

Shi, S., Jung, M. C., Coburn, C., Tadie, A., Sylvinson, D. M. R., Djurovich, P. I., et al. (2019). Highly efficient photo- and electroluminescence from two-coordinate Cu(I) complexes featuring nonconventional N-heterocyclic carbene. *J. Am. Chem. Soc.* 141, 3576–3588. doi: 10.1021/jacs.8b12397

So, O.-K. M., Cheng, G., Wang, J., Chang, X., Kwok, C.-C., Zhang, H., et al. (2017). Efficient color-tunable copper(I) complexes and their applications in solution-processed organic light-emitting diodes. *Chem. Asian J.* 12, 1490–1498. doi: 10.1002/asia.201700081

Tang, C. W., and VanSlyke, S. A. (1987). Organic electroluminescent diodes. *Appl. Phys. Lett.* 51, 913–915. doi: 10.1063/1.98799

To, W.-P., Zhou, D., Tong, G. S. M., Cheng, G., Yang, C., and Che, C.-M. (2017). Highly luminescent pincer gold(III) aryl emitters: thermally activated delayed fluorescence and solution-processed OLEDs. *Angew. Chem. Int. Ed.* 129, 14036–14041. doi: 10.1002/anie.201707193

Uoyama, H., Goushi, K., Shizu, K., Nomura, H., and Adachi, C. (2012). Highly efficient organic-light-emitting diodes from delayed fluorescence. *Nature 492*, 234–238. doi: 10.1038/nature11687

Vezzu, D. A. K., Deaton, J. C., Jones, J. S., Bartolotti, L., Harris, C. F., Marchetti, A. P., et al. (2010). Highly luminescent tetradentate bis-cycloometalated platinum complexes: design, synthesis, structure, photophysics, and electroluminescence application. *Org. Chem.* 49, 5107–5119. doi: 10.1021/oc1002266

Volz, D., Chen, Y., Wallesch, M., Liu, R., Féchner, C., Zink, D. M., et al. (2015). Bridging the efficiency gap: fully bridged dinuclear Cu(I) complexes for singlet harvesting in high-efficiency OLEDs. *Adv. Mater.* 27, 2538–2543. doi: 10.1002/adma.201405897

Wenger, O. S. (2018). Photoactive complexes with earth-abundant metals. *J. Am. Chem. Soc.* 140, 13522–13533. doi: 10.1021/jacs.8b08822

Wong, B. Y.-W., Wong, H.-L., Wong, Y.-C., Chan, M.-Y., and Yam, V.-W. (2017). Versatile synthesis of luminescent tetradentate cyclooctatetraaluminium alkynylgold(III) complexes and their application in solution-processable organic light-emitting devices. *Angew. Chem. Int. Ed.* 56, 302–305. doi: 10.1002/anie.201607816

Wong, M. Y., and Zysman-Colman, E. (2017). Purely organic thermally activated delayed fluorescence materials for organic light-emitting diodes. *Adv. Mater.* 29, 12374–12385. doi: 10.1002/adma.201605444

Yang, Z., Mao, Z., Xie, Z., Zhang, Y., Liu, S., Zhao, J., et al. (2017). Recent advances in organic thermally activated delayed fluorescence materials. *Chem. Soc. Rev.* 46, 915–1016. doi: 10.1039/C6CS0368K
Yersin, H., Czerwieniec, R., Shafikov, M. Z., and Suleymanova, A. F. (2017). TADF material design: photophysical background and studies focusing on CuI and AgI complexes. ChemPhysChem 18, 3508–3535. doi: 10.1002/cphc.201700872

Yersin, H., Rausch, A. F., Czerwieniec, R., Hofbeck, T., and Fischer, T. (2011). The triplet state of organo-transition metal compounds. Triplet harvesting and singlet harvesting for efficient OLEDs. Coord. Chem. Rev. 255, 2622–2652. doi: 10.1016/j.ccr.2011.01.042

Yeung, K.-T., To, W.-P., Sun, C., Cheng, G., Ma, C., Tong, G. S. M., et al. (2017). Luminescent tungsten(VI) complexes: photophysics and applicability to organic light-emitting diodes and photocatalysis. Angew. Chem. Int. Ed. 56, 133–137 doi: 10.1002/anie.201608240

Zhang, J., Duan, C., Han, C., Yang, H., Wei, Y., and Xu, H. (2016). Balanced dual emissions from tridentate phosphine-coordinate copper(I) complexes toward highly efficient yellow OLEDs. Adv. Mater. 28, 5975–5979. doi: 10.1002/adma.201600487

Zhang, Q., Komino, T., Huang, S., Matsunami, S., Goushi, K., and Adachi, C. (2012). Triplet exciton confinement in green organic light-emitting diodes containing luminescent charge-transfer Cu(I) complexes. Adv. Funct. Mat. 22, 2327–2336. doi: 10.1002/adfm.201101907

Zhou, D., To, W.-P., Kwak, Y., Cho, Y., Cheng, G., Tong, G. S. M., et al. (2019). Thermally stable donor-acceptor type (alkynyl)gold(III) TADF emitters achieved EQEs and luminance of up to 23.4% and 70 300 cd m−2 in vacuum-deposited OLEDs. Adv. Sci. 2019:1802297. doi: 10.1002/advs.201802297

Zhou, D., To, W.-P., Tong, G. S. M., Cheng, G., Du, L., Phillips, D. L., et al. (2020). Tetradentate gold(III) complexes as thermally activated delayed fluorescence (TADF) emitters: microwave-assisted synthesis and high-performance OLEDs with long operational lifetime. Angew. Chem. Int. Ed. 59, 6375–6382. doi: 10.1002/anie.201914661

Zhu, Z.-Q., Fleetham, T., Turner, E., and Li, J. (2015). Harvesting all electrogenerated excitons through metal assisted delayed fluorescent materials. Adv. Mater. 27, 2533–2537. doi: 10.1002/adma.201401772

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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