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Zinc complexes exhibiting highly efficient thermally activated delayed fluorescence and their application to organic light-emitting diodes[†]

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Metal complexes emitting thermally activated delayed fluorescence based on intra-ligand charge transfer and enhanced by metallization were synthesized. Organic lightemitting diodes using a thermally stable zinc complex processed by vacuum vapor deposition achieved an external quantum efficiency of nearly 20%.

Since Tang and VanSlyke reported a multilayered organic electroluminescent (EL) device in 1987,¹ the development of organic light-emitting diodes (OLEDs) has rapidly progressed. Their thinfilm active layers, low driving voltages, high efficiencies, and vivid RGB emission make OLEDs especially attractive for application in various kinds of flat-panel displays such as mobile phones and televisions, and they are also expected to find uses in solid-state lighting. Significant advances in light emission efficiency were made through the development of room temperature phosphorescence materials such as heavy metal complexes containing Ir, Pt, Ru, Os and Au, resulting in internal EL quantum efficiencies (η_{int}) of nearly 100%.²⁻⁴ Recently, we followed a new route based on the phenomenon of thermally activated delayed fluorescence (TADF) to achieve the ultimate η_{int} of 100% using rather simple aromatic compounds having no precious metals, beginning the third generation of OLEDs. To develop TADF materials, we designed molecules with the goal of reducing the energy difference between singlet (S₁) and triplet (T₁) excited states (ΔE_{ST}). We determined that separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is fundamental to reducing $\Delta E_{\rm ST}$. Based on this guideline, we developed and reported a series of high-performance light emitters in this new class of 2-biphenyl-4,6-bis(12-phenylindolo[2,3materials. such as a]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ),⁵ phenoxazinetriphenyltriazine (PXZ-TRZ),⁶ and 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN).⁷

While TADF materials comprised entirely of conventional carbon-based aromatic compounds are possible, metallization of aromatic compounds is expected to have advantages such as improved thermal stability due to higher molecular weight and an enhancement of the intersystem crossing (ISC) rate ($k_{\rm ISC}$).⁸⁻¹⁰ In fact, interestingly, metal complexes with rather light metals such as Al, Ga, and In have been reported to have increased $k_{\rm ISC}$ because of a

weak heavy-atom effect.^{11,12} On the other hand, the external heavyatom effect of bromine is well established to be responsible for a significant increase in the rates of ISC, reverse ISC (k_{RISC}), and radiative decay.¹³ Based on these previous studies, we focused on an advanced molecular design for improving TADF characteristics by complexation with light metals such as Al and Zn. Previously, TADF from metal complexes has been reported for copper complexes using σ - π * transitions with charge-transfer character, resulting in a rather high maximum external quantum EL efficiency of $\eta_{\text{ext}} = 17.7\%$.¹⁴ However, copper complexes generally lack thermal and electrochemical stability, motivating us to develop other metal complexes.¹⁵

Herein, we report novel TADF materials based on metal complexes containing aluminum or zinc. Figure 1 shows the molecular structures of the metal complexes synthesized in this study. At first, we focused on the well-known aluminum complex bis(2-methyl-8-quninolinato)-4-phenylphenolate (BAlq) as a prototypical backbone structure having two different ligands.¹⁶ Because of its rather large $\Delta E_{\rm ST} = 0.5 {\rm eV}$,¹⁷ we introduced the electron-donating group triphenylamine (TPA-OH)¹⁸ in place of 4-phenylphenol and the electron-accepting group phenylbenzoxazole (BOX-OH) in place of 2-methyl-8-quinolinol, as shown in Fig. 1(a) (Al-1).¹⁹ We calculated the HOMO and LUMO and estimated $\Delta E_{\rm ST}$ through density functional theory (DFT) calculations and studied the electronic transitions with time-dependent DFT (TD-DFT) calculations.^{20,21} The calculations were performed using a Gaussian 09 program package²² at the PBE0/def2-SV(P) level.^{23,24} While the



Fig. 1 (a) Molecular structures. (b) HOMO and LUMO of complex Zn-1.

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calculations predicted well-separated HOMO and LUMO and a small $\Delta E_{\rm ST}$ value of 0.0063 eV (Fig. S1 and Table S1), the $\Delta E_{\rm ST}$ of Al-1 in 2MeTHF solution was experimentally found to be rather large (0.50 eV), resulting in no appearance of delayed fluorescence (Fig. S2). Since the phosphorescence spectrum of Al-1 was observed to be similar to that of BOX-OH (Fig. S2(b)), we concluded that the emission process is dominated by intra-ligand charge transfer (ILCT) on BOX-OH. While the calculation of Al-1 suggests that the transitions from S_1 and T_1 are mainly due to LLCT, the spectral characteristics clarified that the phosphorescence has vibrational modes, indicating that the transition can be ascribed to ILCT. Thus, we suppose that T1, T2, S1 and T2 transitions are basically prohibited and the lowest transition occurs from the T₃ level. Also, we confirmed that the triplet energy level of BOXOH is lower than that of TPAOH. Thus, we concluded the phosphorescence emission is due to ILCT in BOXOH. This is supported by the value of $\Delta E_{\rm ST}$ = 0.375 eV ($\Delta E_{ST} = E_{S3} - E_{T3}$) for ILCT obtained by TD-DFT calculations (Table S1), which is in good agreement with the experimentally obtained value.

From these results, we concluded that tuning the ILCT transition can be a route to induce TADF in some metal complexes. Thus, we designed the advanced molecular structure Al-2, in which the BOX-OH ligands are replaced with 2-(benzo[d]oxazol-2-yl)-5-(10Hphenoxazin-10-yl)phenol (PX-BOX-OH) ligands comprised of the electron-accepting unit BOX-OH and the electron-donating unit phenoxazine (PX),²⁵ to enhance intra-ligand charge transfer. Quantum chemical calculations show that S₁ and T₁ are determined by the ILCT, and ΔE_{ST} was revealed to be as small as 0.0146 eV (Table S1 and Fig. S1). Furthermore, we designed Zn-1 and Zn-2, which have PX in the R₂ and R₃ positions, respectively (Fig. 1(a)). As a reference, we synthesized **OMe-1**, which has a methyl substituent instead of the metal coordination (Fig. 1(a)). Quantum



chemical calculations for **Zn-1** and **Zn-2** show that their S_1 and T_1 can be attributed to ILCT and that their ΔE_{ST} are very small, with values of 0.0174 eV and 0.0371 eV, respectively (Fig. S3 and Table S2). Thus, we expected these materials to exhibit TADF. Furthermore, the calculated HOMO and LUMO for **Zn-1** in Fig. 1(b) show that the HOMO is localized in PX and the LUMO is localized in BOX, confirming our idea that the radiative transition can be mainly attributed to ILCT and that the metal orbital contribution is weak.

We synthesized the ligands and complexes based on a conventional procedure, the details of which are provided in the supplementary information. We note that, in the case of Al-2, the formation of a dimer structure,²⁶ Al-2' as shown in Fig. 2, was confirmed by MALDI-TOF-MS and that we could not synthesize the



Fig. 3 (a) Absorption and emission spectra in toluene solutions. (b) Transient PL decay at 300 K for films of Zn-1, Zn-2, or OMe-1 doped into mCBP at a concentration of 6 wt%.

target material. We measured TG-DTA of Al-2' and Zn-1 under reduced pressure and atmosphere to examine their thermal stability (Fig. S4). The TG-DTA of Al-2' showed an appreciable weight loss with rising temperature due to ligand elimination and a residual substance with a weight of 10% of the initial, indicating thermal instability and decomposition. On the other hand, Zn-1 showed a rapid weight loss only above 310 °C and no residual material, suggesting good thermal stability. Thus, we purified Zn-1, and additionally Zn-2 and OMe-1, by train sublimation before studying their properties in films and devices.

Photoluminescence (PL) and phosphorescence spectra of Al-2' were measured in 2MeTHF solutions (Fig. S5(a)). The peak of the fluorescence spectrum of Al-2' was around $\lambda_{\rm F} = 522$ nm, and the phosphorescence spectrum was similar to that of PX-BOX-OH (Fig. S5 (b)), indicating that the origin of the emission is ILCT. We estimated a $\Delta E_{\rm ST}$ of 0.06 eV from the difference between the onsets of the fluorescence and phosphorescence spectra (Fig. S5(a)). Since Al-2' is thermally unstable, we fabricated a 6-wt%-doped thin film with 1,3-bis(N-carbazolyl)benzene (mCP) as host by spin-coating. In the doped film, the emission peak wavelength was observed at 530 nm, and the PL quantum yield was $\phi_{\rm PL} = 86.7\%$. We also confirmed that the delayed component of emission gradually increases with temperature (Fig. S6).

On the other hand, since the zinc complexes were thermally stable, we fabricated 6-wt%-doped thin films with 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) as host by vacuum vapor deposition. While $\lambda_{\rm F}$ of **Zn-1** and **Zn-2** in toluene solutions were 560 nm and 540 nm (Fig. 3(a)), respectively, they significantly blue shifted in 6 wt% doped films to 542 nm and 525 nm, respectively (Fig. S7). We can attribute the blue shift to the change in the substituent from the para (**Zn-1**) to the meta (**Zn-2**) position, which also leads to a decrease in $\phi_{\rm PL}$. The detailed spectral characteristics including **OMe-1** are summarized in Table 1. From the spectral data (Fig. S8), we obtained a $\Delta E_{\rm ST}$ for **Zn-1** (0.31 eV), indicating that the complexation effectively reduces $\Delta E_{\rm ST}$.

Transient PL decay curves show the clear presence of prompt and delayed components. Transient decay times for the prompt and delayed components of $\tau_p = 12.8 \pm 0.4$ ns and $\tau_d = 37.8 \pm 2.5$ µs, respectively, were observed for **Zn-1**, and the delayed fluorescence component increased with rising temperature for all materials (Fig. S8). The ϕ_{PL} for **Zn-1**, **Zn-2**, and **OMe-1** were about 78.4%, 58.2%

Table 1 Photoluminescence properties in mCBP films doped with 6 wt% emitter											
Emitter	$\lambda_{\rm F}$ (nm)	φ _{PL} (%)	ϕ_{F}^{a} (%)	ϕ_{TADF} (%)	$\Delta E_{\rm ST}$ (eV)	$k_{\rm ISC}$ (s ⁻¹)	k_{RISC} (s ⁻¹)				
Zn-1	542	78.4	12.3	66.1	0.06	0.6×10^{8}	16.9×10^{4}				
Zn-2	523	58.2	10.1	48.1	0.18	$0.5 imes 10^8$	$1.4 imes 10^4$				
OMe-1	490	63.0	4.7	58.3	0.31	1.9×10^{8}	$0.7 imes 10^4$				
^{<i>a</i>} Prompt fluorescence comr	ponent of $\phi_{\rm Pl}$										

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and 63%, respectively, and all three materials exhibited efficient TADF with quantum yields (ϕ_{TADF}) around 50-60% (Table 1). Although no significant difference in ϕ_{PL} was observed by metallization, the PL decay lifetime dramatically decreased for **Zn-1** compared to **Zn-2** and **OMe-1** (Fig. 3(b)). By estimating k_{RISC} and k_{ISC} using Eq. S1,²⁷ we found that k_{RISC} increases and k_{ISC} roughly decreases for the compounds in the order **OMe-1** \rightarrow **Zn-2** \rightarrow **Zn-1** (Table 1), with k_{RISC} of **Zn-1** increasing approximately 25 times and k_{ISC} decreasing about two-thirds compared to **OMe-1**. Here, while the metal orbital did not affect the transition between the HOMO and LUMO as indicated by quantum chemical calculations, the metallization clearly reduced ΔE_{ST} . We attribute this to the complexation changing the angle of the donor and the acceptor, resulting in a smaller ΔE_{ST} and an increase of k_{RISC} .

Finally, we discuss the performance of OLEDs using the metal complexes as emitters. In the case of Al-2', we used mCP as the host



Fig. 4 (a) The η_{ext} -*J* characteristics and (b) *J*-voltage (*V*)-luminance (*L*) characteristics for OLEDs with **Zn-1**, **Zn-2**, or **OMe-1** as emitter.

in a device with the structure of indium-tin-oxide (ITO)/ poly(3,4ethylene-dioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/ 6 ± 1 wt% Al-2': mCP (20 nm)/ 1,3,5-tris(Nphenylbenzimidazol-2-yl)benzene (TPBi, 55 nm)/ LiF (0.8 nm)/ Al (80 nm). The maximum η_{ext} was 6.81% at a current density (*J*) of 0.26 mA/cm² (Fig. S10). Assuming a light outcoupling efficiency of $\eta_{out} \approx 20\%$,²⁸ η_{int} was estimated from experimental η_{ext} to be 34% (Eq. S2), which is higher than the theoretical limit of 25% in conventional fluorescence-based OLEDs.

On the other hand, in the cases of Zn-1 and Zn-2, we prepared devices with the structure ITO/ 4,4'-bis[N-(1-naphtyl)-Nphenylamino]biphenyl (α -NPD, 35nm)/ 6 ± 1 wt% emitter: mCBP (15 nm)/ TPBi (65 nm)/ LiF (0.8 nm)/ Al (80 nm) (Fig. S11). Due to the shorter wavelength emission characteristics of OMe-1, we used DPEPO as the host and the following device structure: ITO/ α -NPD (35 nm)/ mCP $(10 \text{ nm})/6 \pm 1 \text{ wt\%}$ **OMe-1**: DPEPO (15 nm)/DPEPO (10 nm)/ TPBi (30 nm)/ LiF (0.8 nm)/ Al (80 nm). As shown in Fig. 4, **Zn-1** demonstrated the highest $\eta_{\text{ext}} = 15\%$ at J =0.05 mA/cm², while **Zn-2** and **OMe-1** exhibited $\eta_{\text{ext}} = 10.4\%$ at J =0.01 mA/cm² and $\eta_{\text{ext}} = 8.5\%$ at J = 0.01 mA/cm², respectively. The η_{int} , assuming $\eta_{\text{out}} \approx 20\%$, were estimated from experimental η_{ext} to be 75.6% (Zn-1), 52.0% (Zn-2) and 42.5% (OMe-1), which are higher than the theoretical limit of 25% for conventional fluorescence. Also, we observed relaxation of the roll-off of efficiency at high current densities in the Zn-1-based OLED



Fig. 5 Transient PL decay at 300 K for films of Zn-1, Mg-1, or Li-1 doped into mCBP at a concentration of 6 wt%.

compared to the other devices, which would be reasonably expected based on the small ΔE_{ST} and large k_{RISC} of **Zn-1** improving upconversion efficiency and relaxing exciton annihilation arising from exciton-exciton and exciton-polaron interactions.

We further examined the effect of the central metal on the optical and OLED characteristics by synthesizing complexes with magnesium (**Mg-1**) and lithium (**Li-1**) using the same ligands as **Zn-1** (Fig. 1(a)). We fabricated doped thin films composed of mCBP as host material and the emitters in a dopant concentration of 6 wt%. The λ_F (Fig. S12) and ϕ_{PL} were 522 nm and 70.6% for **Mg-1** and 510 nm and 70.4% for **Li-1**, respectively. The fluorescence peak wavelength blue shifted from **Mg-1** to **Zn-1** although their ϕ_{PL} were almost the same (Table 2). The ΔE_{ST} of **Zn-1** was the smallest of all



Fig. 6 (a) The η_{ext} -J characteristics and (b) J-V-L characteristics for OLEDs with **Zn-1**, **Mg-1**, or **Li-1** as emitter in devices with the structure ITO/ α -NPD (35 nm)/ 6 ± 1 wt% emitter: mCBP (30 nm)/ TPBi (50 nm)/ LiF (0.8 nm)/ Al (80 nm). The inset of (a) shows the normalized EL intensity of the devices at 10 mA/cm².

of the materials (0.08 eV for **Mg-1** and **Li-1**) (Fig. S13). The PL decay lifetimes were seen to decrease in the order **Li-1** > **Mg-1** > **Zn-1** (Fig. 5). Based on the analysis of kinetic rates, we found a systematic atomic-number effect in these complexes (Fig. S14). In typical metal complexes of conventional fluorescent materials, spin-orbit coupling promotes $k_{\rm ISC}$ with increasing atomic number, eventually leading to a decrease of fluorescence quantum yield. However, in these TADF complexes, $k_{\rm RISC}$ values were enhanced while $\phi_{\rm PI}$ were constant.

We fabricated OLEDs using these complexes in devices with the structure as follows: ITO/ α -NPD (35 nm)/ 6 ± 1 wt% emitter: mCBP (30 nm)/ TPBi (50 nm)/ LiF (0.8 nm)/ Al (80 nm). The **Zn-1**

Table 2 Photoluminescence properties of mCBP films doped with 6 wt% emitter and key OLED characteristics of devices with the structure ITO/ α -NPD (35 nm)/ 6 ± 1 wt% emitter: mCBP (30 nm)/ TPBi (50 nm)/ LiF (0.8 nm)/ Al (80 nm)

Emitter	$\lambda_{ m F}$	$\phi_{ m PL}$	$\phi_{ m F}$	$\phi_{ ext{TADF}}$	$\Delta E_{ m ST}$	$\eta_{ ext{int}}{}^a$	$\eta_{\mathrm{ext, calc}}{}^a$	$\eta_{\mathrm{ext, exp.}}^{b}$
	(nm)	(%)	(%)	(%)	(eV)	(%)	(%)	(%)
Zn-1	542	78.4	12.3	66.1	0.06	76.1	15.2	19.6
Mg-1	516	70.6	13.1	57.5	0.08	67.3	13.4	16.5
Li-1	510	70.4	7.6	62.8	0.08	68.6	13.7	12.9
⁴ Theoretical off	iaianaias anlau	lated using Eq	S2 with the tel	bulated experiment	al DL abarratoristics	and $m \sim 20\%^{-b}$	Evnorimontal mavir	12.9

device demonstrated $\eta_{\text{ext}} = 19.6\%$ at $J = 0.11 \text{ mA/cm}^2$, while the **Mg-1** and **Li-1** devices showed $\eta_{\text{ext}} = 16.5\%$ at $J = 0.06 \text{ mA/cm}^2$ and $\eta_{\text{ext}} = 12.9\%$ at $J = 0.05 \text{ mA/cm}^2$, respectively (Fig. 6). The calculated η_{ext} , assuming $\eta_{\text{out}} \approx 20\%$, were estimated to be 15.2% (**Zn-1**), 13.4% (**Mg-1**) and 13.7% (**Li-1**). The experimentally obtained η_{ext} showed slightly higher values of 19.6% (**Zn-1**) and 16.5% (**Mg-1**), suggesting the contribution of molecular orientation (Table 2, Eq. S2).

In summary, we synthesized new TADF materials based on metal complexes having ILCT transition. The new metal complexes showed good thermal stability for the fabrication of thin films by vacuum vapor deposition. Furthermore, we realized the reduction of $\Delta E_{\rm ST}$ and enhancement of $k_{\rm RISC}$ by metallization. The OLEDs using **Zn-1** achieved very high $\eta_{\rm ext}$ close to 20%.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and synthesis details, additional photophysical data, and supplementary figures and tables. See DOI: 10.1039/c000000x/

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