



Optoelectronic Materials

A Zinc(II) Benzamidinate *N*-Oxide Complex as an Aggregation-Induced Emission Material: toward Solution-Processable White Organic Light-Emitting Devices

Mihela Cibian,^[a] Afshin Shahalizad,^[b] Fathi Souissi,^[b,c] Jessica Castro,^[a] Janaina G. Ferreira,^[a] Daniel Chartrand,^[a,d] Jean-Michel Nunzi,^{*[b]} and Garry S. Hanan^{*[a]}

Abstract: The synthesis, characterization, photophysical and redox properties of a dinuclear complex $Zn_2(AMOX)_4$ (AMOX = 4-bromo-*N*,*N'*-diphenylbenzamidinate *N*-oxide) are highlighted. This compound is a first example of a novel class of aggregation-induced emission (AIE) materials. Noticeably, solution-processed white-green organic light-emitting diodes were fabricated using this complex as dopant in a co-host matrix in the

Introduction

Over the last decade, researchers have been motivated to improve the photophysical and morphological properties of compounds used in optoelectronic applications in order to increase the performance efficiency of the devices and to reduce their production cost.^[11] In this regard, aggregation-induced emission (AIE) materials^[2] present great potential for the development of solid-state optoelectronic technologies such as organic lightemitting diodes (OLEDs).^[2c] While the first AIE compounds were entirely organic aromatic compounds,^[3] AIE materials based on coordination complexes have been developed more recently.^[2c,4] The latter category presents additional advantages brought by the metal ions, such as enhanced thermal and environmental stability, the possibility of a synergic double contribution for electron/hole transport and increased light emission.^[2c,4,5]

Coordination complexes of anionic, bidentate N,O-ligands [e.g., 2-(2-benzothiazolyl)phenolate (BTZ),^[6] 2-(2-benzoxazolyl)-

[a]	Département de Chimie, Université de Montréal,
	2900 Edouard-Montpetit, Montréal, Québec, H3T-1J4, Canada,
	E-mail: garry.hanan@umontreal.ca
	www.greenenergygroup.ca
[b]	Department of Physics, Engineering Physics and Astronomy,
	Queen's University,
	Kingston, Ontario, K7L 3N6, Canada,
	E-mail: nunzijm@queensu.ca
	http://faculty.chem.queensu.ca/people/faculty/Nunzi/
[c]	Laboratory of Nanomaterials and Systems for Renewable Energies
	(LaNSER), Center for Research and Technologies of the Energy Technopole,
	Borj Cedria, Bp 95,
	Hammam Lif, 2050, Tunisia
[d]	Present address: LAMP - Laboratoire d'Analyse pour les Molécules et
	Matériaux Photoactifs - Laboratory for the Analysis of Molecules' and
	Materials' Photoactivity, Université de Montréal, Canada
닖	Supporting information and ORCID(s) from the author(s) for this article and

a supporting mornation and oricity(s) non-the datalor(s) for this drifte dre **a**vailable on the WWW under https://doi.org/10.1002/ejic.201800579. emissive layer. A luminance efficiency and power efficiency as high as 1.12 cd/A and 0.30 lm/W were obtained, respectively. The characteristics of this complex: high solubility, thermal stability, AIE behaviour, ease of synthesis, tunability options, and low-cost, reveal altogether great potential for the development of this new family of compounds as materials for applications in optoelectronic devices.

phenolate,^[7] quinolin-8-olate^[8] (q), 2-pyridylcarboxylate^[9]] with metal ions such as Ir^{III [9,10]} Al^{III [7,8,11]} and Zn^{II[6a–6c,7,8b,8d,11a,12]} have been successfully used in optoelectronic devices.^[13] Of these metal ions, the latter has attracted increased interest as it is biocompatible, earth-abundant, and inexpensive, especially when compared with iridium.^[6,7,8b,8d,11a,12a,14] Zn^{II} complexes which exhibit AIE behavior have also been reported.^[4,15] In particular, zinc(II) complexes have been targeted for fabrication of low-cost single-compound white organic light-emitting diodes (WOLEDs) as illumination sources^[16] due to their broad emission bands and good charge transport properties.^[11a,17] They have been employed as host materials for phosphorescent emitters and also as charge transport layers in a variety of OLED structures.^[6a,6d,18] It is important to note that those devices were fabricated by thermal evaporation which is a complex process requiring expensive infrastructure. Solution-processing is technically less complicated, inexpensive, and therefore highly attractive for large-area manufacturing purposes.^[19] However, to date, reports on solution-processed zinc(II) complex-based OLEDs are scarce.^[20] Moreover, to the best of our knowledge, there has been no report on solution-processed WOLEDs based on zinc(II) complexes with AIE behavior.

Part of our ongoing research on coordination compounds focuses on amidine *N*-oxides (AMOXs, also called α -aminonitrones and *N*-hydroxyamidines) and their transition metal complexes. AMOXs are anionic, bidentate N,O-ligands and are good chelators for metal ions. They exhibit extended conjugation in the amidine backbone, structural rigidity, and present the possibility to introduce *C*-aryl and *N*,*N'*-diaryl substituents,^[21] key features as platforms for AIE materials.^[2] Here, we report the synthesis and characterization of the dinuclear O-bridged complex Zn₂(AMOX)₄ (**1**) (AMOX = 4-bromo-*N*,*N'*-diphenylbenzamidinate *N*-oxide) (Figure 1), which opens the route to a new class of materials exhibiting AIE behaviour. The performance of



solution-processed OLEDs using **1** as the dopant in the EML was also investigated and is discussed herein.

Results and Discussion

Synthesis and Characterization

The synthesis of **1** is outlined in Scheme 1. The parent benzamidine AM (4-bromo-N,N'-diphenylbenzamidine)^[22] was prepared in excellent yield (97 %) by condensation of the 4-bromobenzoic acid with two equivalents of aniline, in polyphosphoric acid trimethylsilyl ester (PPSE), at 180 °C, followed by basic treatment.^[23] N-Oxidation of **AM** with *meta*-chloro-peroxybenzoic acid (m-CPBA) in dichloromethane (DCM) at room temperature (r. t.) afforded the AMOX ligand in reasonable yield (51 %).^[24] The reaction of zinc(II) acetate with two equivalents of AMOX in aqueous ethanol at r. t. readily gave a precipitate, the dimeric complex 1, which was isolated in good yield (70 %) as an air-stable yellow powder. Both 1 and AMOX were characterized by ¹H NMR and ¹³C NMR spectroscopy, mass spectrometry (MS) (Figure S1-S3, SI), and elemental analyses (EA). Complex 1 has a good thermal stability, the decomposition temperature (T_{d}) at 5 % weight loss being 243 °C. (Figure S4, SI).

The solid-state structure of **1** is presented in Scheme 1 (inset) and Figure S5–S7, SI. XRD quality single crystals were grown from slow evaporation of a DCM/hexane solution of the compound at -10 °C. Crystal data and refinement details are given in Table S1, SI. Selected bond lengths and angles are tabulated in Table 1.



Figure 1. Frontier molecular orbitals (MOs) for **1** [isovalue at 0.03; occupied orbitals in green and virtual orbitals in pink; theory level: B3LYP/6,31-g(d,p), PCM: DCM].



Complex **1** crystalized in the $P2_1/c$ space group, as a DCM solvated dimer [**1·3(CH₂Cl₂)**]. The center of the dimer and one of the solvent molecules sit on inversion centers. Similar dimeric structures exist for the complexes of zinc(II) with the BTZ ligand [Zn(BTZ)₂]₂,^[6b] as well as with substituted q ligands [Zn(Rq)₂]₂.^[25] Trimeric and tetrameric structures are also reported for the latter.^[8b,26] The solid-state structure of **1·3(CH₂Cl₂)** highlights pentacoordinate zinc(II) centres with a distorted square-pyramidal geometry ($\tau_5 = 0.20$).^[27] The Zn···Zn distance of 3.092(1) Å is comparable but at the lower limit of those found in [Zn(Rq)₂]₂ and [Zn(BTZ)₂]₂ (3.06–3.29 Å) (Table 1).

The AMOX ligands show two coordination modes to the zinc(II) ions: μ-AMOX-κN,κO:κO and AMOX-κN,κO. The Zn-O bond lengths for the bridging AMOX ligands [2.152(2) and 2.076(2) Å] are longer than those in the non-bridging ones [1.966(2) Å], indicating, as expected, weaker interactions between the zinc(II) centers and the bridging O atoms. However, the Zn-N distances [2.073(2) Å and 2.075(2) Å] are statistically identical in both types of AMOX ligands. For comparison, selected bond lengths and angles in 1 and those in the $[Zn(BTZ)_2]_2$ and $[Zn(^Rq)_2]_2$ dimers are shown in Table 1. In terms of packing forces, in the solid-state structure of 1-3(CH₂Cl₂), intramolecular [C(C-aryl)-H--O] and intermolecular [C(DCM)-H---Br; C(C-aryl)-H---Cl] hydrogen bonds exist (Figure S6, ESI[,] SI), as well as networks of intermolecular C(sp2)–H··· π C(sp2) and Br... π C(sp2) interactions (Figure S7, SI). The latter patterns were also identified in other AIE compounds.[34] The existence of the dimeric form of the compound in the solid bulk powder was confirmed by X-ray powder diffraction analyses (Figure S8, SI). A distinction should be made between the molecular complex 1 in powder form which does not contain solvent molecules (1), the single crystals of 1 containing co-crystalized solvent [1-3(CH₂Cl₂)], and the sample of crushed and dried crystals used for the comparison with the powder sample in the X-ray powder diffraction experiments.

Redox and Photophysical Properties

The electrochemical and photophysical data for **1** are tabulated in Table 2, together with experimental data for $[Zn(BTZ)_2]_2^{[6a,6b,6d]}$ and $[Znq_2]_4$,^[8d,31–33] molecular luminescent materials which have been successfully used in OLEDs. Cyclic voltammetry measurements for **1** in DCM show two irreversible ligand-based oxidation events at 0.97 V and 1.16 V vs. SCE. No reduction event is observed in the solvent window, in line with the anionic character of the AMOX ligand, as also found for zinc(II) complexes with bulky formamidinate *N*-oxides.^[35] The electronic spectrum of **1** (Figure S10, SI and Table 2) features π - π * ligand-centred transitions. The lowest-energy transitions present a λ_{max} at 336 nm with ε = 38800 m⁻¹ cm⁻¹. DFT and TD-DFT studies [vide infra; theory level: B3LYP/6,31-g(d,p), PCM: DCM] were undertaken in order to better understand the electronic properties of the complex.

The molecular orbital (MO) manifold for **1** is influenced by the symmetry of the molecule (inversion center at the center of the dimer), resulting in symmetry-related pairing (Figure 1 and Figure S9, SI). The degenerate HOMO/H-1 are mainly local-







Scheme 1. Synthesis of the zinc(II) dinuclear complex 1 (AM = the 4-bromo- $N_{r}N'$ -diphenylbenzamidine precursor, AMOX = 4-bromo- $N_{r}N'$ -diphenylbenzamidinate N-oxide ligand; PPSE = polyphosphoric acid trimethylsilyl ester); the inset is showing the ORTEP view of 1-3(CH₂Cl₂) with ellipsoids drawn at 50 % probability level. Hydrogen atoms and co-crystallized DCM molecules have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **1-3(CH₂Cl₂)** (from its solid-state structure and its DFT optimized structure), and for selected relevant zinc(II) complexes from the literature.^[28]

Cpd.	$\tau_{5}^{[g]}$	Bond length	ıs [Å]		Angles					
		Zn1-01	Zn1010	Zn1-010 ^[i]	Zn1–N2	Zn1-N4	Zn•••Zn			
1-3(CH ₂ Cl ₂)	0.20	1.996(2)	2.152(2)	2.076(2)	2.075(2)	2.073(2)	3.092(1)	Zn1–O10–Zn1 ^[i]	O10-Zn1-O10 ^[i]	01-Zn1-N2
[Zn(BTZ)₂]₂ ^[a]	0.87	1.962(2)	2.058(2)	2.016(2)	2.095(3)	2.170(3)	3.209(1)	94.0(1)	86.0(1)	79.6(1)
[Zn(^R q) ₂] ₂ -1 ^[b]	0.19	1.978(3)	2.105(2)	2.085(3)	2.095(4)	2.047(3)	3.060(1)	103.9(1)	76.1(1)	87.4(1)
[Zn(^R q) ₂] ₂ -2 ^[c]	0.58	1.959(2)	2.090(2)	2.023(2)	2.131(3)	2.222(3)	3.243(1)	93.8(1)	86.2(1)	81.8(1)
[Zn(^R q) ₂] ₂ -3 ^[d]	0.20 and 0.47 ^[h]	1.978(3) ^[i]	2.118(3)-2.144(3) ^[j]	2.006(4) ^[i]	2.051(2)-2.113(2) ^[j]	2.191(4) ^[i]	3.291(1)	104.1(1)	74.9(1)	82.7(1)
[Zn(^Rq)₂]₂-4 ^[e]	0.54	1.954(4)	2.022(4)	2.078(4)	2.134(4)	2.140(5)	3.262(1)	104.7(1)-106.0(1) ^[j]	74.4(1) ^[i]	82.3(1)-84.4(1) ^[j]
1-dft ^[f]	0.30	1.98	2.20	2.06	2.13	2.06	3.22	105.4(2)	74.6(2)	82.7(2)

[a] $[\mathbf{Zn}(\mathbf{RTZ})_2]_2$ [BTZ = 2-(2-benzothiazolyl)phenolate]^(6b). [b] $[\mathbf{Zn}(^{\mathbf{R}}\mathbf{q})_2]_2$ -1: $^{\mathbf{R}}\mathbf{q}$ = 5-chloro-7-iodoquinolin-8-olato (DOBNEP).^[25b] [c] $[\mathbf{Zn}(^{\mathbf{R}}\mathbf{q})_2]_2$ -2: $^{\mathbf{R}}\mathbf{q}$ = 2-[2-(2,6-dichloro-phenyl)vinyl]quinolin-8-olato (CEBLOM).^[25c] [d] $[\mathbf{Zn}(^{\mathbf{R}}\mathbf{q})_2]_2$ -3: $^{\mathbf{R}}\mathbf{q}$ = 2-[2-(4-methoxyphenyl)vinyl]quinolin-8-olato (MIMLIF).^[29] [e] $[\mathbf{Zn}(^{\mathbf{R}}\mathbf{q})_2]_2$ -4: $^{\mathbf{R}}\mathbf{q}$ = 2-nonylquinolin-8-olato (QUBNIK).^[25a] [f] Optimized structure, theory level: B3LYP/6-31g(d, p), PCM: CH₂Cl₂. [g] As defined by Addison.^[27] [h] Different geometries at the two zinc(II) centers. [i] The average value is given when values are statistically (3\sigma) different.

ized on the ONCN moieties of the two non-bridging AMOXs, whereas the LUMO/L + 1 are found delocalized on the NCN moieties and the C-aryl substituents of the two bridging li-

gands. This distinction indicates that the energy of the LUMO can be fine-tuned by modifying the *C*-aryl substituents with EW/ED groups. The TD-DFT calculations for **1** (Figure S10, Table





Table 2. Photophysical, electrochemical and theoretical data for 1, and selected experimental data for well-established Zn-based compounds for OLED fabrication.

	Experimental data									
Cpd.	λ _{max abs} [nm] (ε x 10² [M ⁻¹ cm ⁻¹])	λ _{max PL} [nm]	Ф _{РL} [%]	т [ns]	<i>E_{pa}(irr)</i> [V] <i>vs.</i> SCE	E _{ox_onset} [V]	HOMO/ IP [eV]	LUMO/ E/ [eV]	A E _g (λ _{abs_onset}) [eV] (nm)	
1 [a], [b]	240 (707)sh, 276 (493)sh, 336 (388) ^[a]	556 ^[c]	2 ^{[c], [d]}	< 1 ^[c]	0.97; 1.16	0.85	-5.25 ^[e]	-2.19 ^{[f], [g]}	3.06 ^[h] (405)	
[Zn(BTZ)2]2 ^[i]	301, 412 ^{[j], [k], [l]}	480 ^[1]	19 ^[1]	24.1 ^[I]	-	-	-5.41 ^{[k], [m]}	-2.65 ^{[g], [k]}	2.76 ^[h] (449)	
[Znq ₂] ₄ ^[n]	379 ^{[0], [p]} / 380 ^{[j], [0]}	542 ^[0]	45 ^[q]	10.3 ^[r]	-	-	-5.54 ^[s]	-2.98 ^[g]	2.56 ^{[h], [o]} (485)	
	Theoretical ^[t] data									
	HOMO ^[u] [eV]				LUMO ^[v] [eV]			<i>E</i> _g (TD-DFT) ^[w] [eV]		
1	-5.08			-1.89			3.19			

[a] Photophysical data were obtained in CH₂Cl₂, at room temperature unless otherwise stated. [b] Electrochemical data were obtained using the following conditions: dry CH₂Cl₂, [*n*Bu₄N]PF₆ 0.1 M, compound concentration about 1 mM, glassy carbon electrode, scan rate 100 mV/s, room temperature, Ar atmosphere, ferrocene used as internal reference; all potentials are reported in volt, vs. SCE (Fc/Fc⁺ vs. SCE was considered 0.46V in DCM^[30]). [c] In solid state (powder). [d] Measured by absolute method, using an integration sphere (error is ± 20 %). [e] HOMO level was determined using the equation: E_{HOMO} (eV) = $-(4.4 + E_{ox_onset})$. [f] No reduction process is observed. [g] LUMO level was determined using the equation: E_{LUMO} (eV) = $E_{HOMO} + E_g$. [h] E_g was obtained using the absorption edge technique: $E_g = 1240/\lambda_{abs_onset}$. [i] BTZ = 2-(2-benzothiazolyl)phenolate. [j] In thin film. [k] From ref.^[6b] [l] From ref.^[6a] [m] Determined by Ultraviolet Photoelectron Spectroscopy (UPS). [n] q = Quinolin-8-olate. [o] From ref.^[8d] [p] In CH₂Cl₂. [q] From ref.^[31] [r] From ref.^[32] [s] From ref.^[33] [t] Theory level: B3LYP/6-31g(d, p), PCM: CH₂Cl₂. [u] HOMO level was obtained from DFT optimization, theory level: B3LYP/6-31g(d, p), PCM: CH₂Cl₂. [v] LUMO level was obtained first singlet, which corresponds to the HOMO–LUMO transition; theory level: B3LYP/6-31g(d, p), PCM: CH₂Cl₂.

S2, SI and Table 2) confirm the lowest energy absorption bands as principally interligand (HOMO/H-1 to LUMO/L + 1 at 384–388 nm), principally intraligand (HOMO/H-1 to L + 2/L + 3 at 371 nm) or mixed inter- and intra-ligand (H-3/H-2 to LUMO/L + 1 at 362–368 nm) transitions. At higher energy, intraligand (HOMO/H-1 to L + 8/L + 9) and mixed inter- and intra-ligand transitions are also calculated (see Table S2, SI).

Furthermore, the theoretical value of the HOMO–LUMO gap of **1** determined by DFT/TD-DFT (3.19 eV) is close to the experimental value (3.06 eV), and it is in the range of those of $[Zn(BTZ)_2]_2^{[6b]}$ and $[Znq_2]_4$,^[8d,31–33] well-established compounds in OLED fabrication (Table 2 and Figure 2).



Figure 2. HOMO–LUMO gap of **1** vs. those of well-established compounds for OLED fabrication: $[Zn(BTZ)_2]_2$ [BTZ = 2-(2-benzothiazolyl)phenolate]^[6b] and $[Znq_2]_4$, (q = quinolin-8-olate).^[8d,36]

Complex **1** is AIE active: it is non-emissive in DCM solution, but it is strongly emissive in the solid state (Figure 3 and Figure S11, SI). Its powder photoluminescence (PL) spectrum features a broad emission band (400–800 nm) with $\lambda_{max em} = 556$ nm at r. t. ($\lambda_{exc} = 350$ nm) (Figure S11, SI). At 77 K, a similar PL spectrum is obtained, with the exception of a narrower bandwidth and a slight blue shift ($\lambda_{max em} = 548$ nm) (Figure S11, SI). The



Figure 3. PL spectra of 1 in hexane/DCM mixtures (concentration: 10^{-4} m; $\lambda_{max\,em} = 556$ nm, $\lambda_{exc} = 350$ nm). Insets show the variation of the PL intensity with the increasing fraction of hexane in the mixture and images of the corresponding solutions under 365 nm UV light; the shoulder peak at 400–450 nm for the emission spectra in this Figure is due to scattering from the experimental setup and it is dissimilar to the shoulder peak observed in the same region in the EL spectra (Figure 4).





AlE behaviour of 1 is shown in Figure 3. PL spectra of 1 in various volumetric fractions of hexane/DCM mixtures are presented (Figure 3). Up to a volumetric ratio of 20 % DCM/ 80 % hexane, complex 1 is non-emissive, but increasing the hexane proportion over 80 % results in formation of emissive aggregates (as suspensions). In general, the AIE behaviour is based on the existence of excited states for which the non-radiative decay pathways are suppressed due to the rigid environment provided by the aggregates restricting their intramolecular rotations.^[2,3,37] Nevertheless, the AIE phenomenon is complex and the understanding and probing of the exact nature of these excited states is yet to be fully established.[37a] Complex 1 has an excited state lifetime τ < 1.0 ns and a photoluminescence quantum yield ($\Phi_{\rm Pl}$) of ca. 2 %, in the solid state (powder). Its short excited state lifetime, the similarity of its PL spectra (powder) at room temp. and 77 K, and those obtained for the AIE experiments, as well as the DFT and TD-DFT calculations, suggest a fluorescence based interligand-type emission. However, the contribution of other luminescence pathways (e.g., intraand intermolecular aromatic-dimer excited states) cannot be excluded, especially considering the broadness of the PL spectrum.[37a]

The short excited state lifetime of **1** in the solid state (powder), together with its broad PL spectrum, and its solubility in common solvents bode well with testing it in solution-processed OLEDs, despite its low photoluminescence quantum yield. EL spectra of the devices A, B, and C were also calculated to be (0.28, 0.51), (0.26, 0.53), and (0.27, 0.54), respectively. Obviously, even though the EL spectra of the devices cover the entire visible spectral region, these color coordinates (particularly the y coordinates) are still far from the ideal values for the ideal white color (0.33, 0.33), due to the narrow bandwidths of the EL spectra. For this reason, the thicknesses of the devices should be optimized in order to avoid undesired microcavity effects and to achieve ideal broad-band white color, which is the subject of our future work.

It should also be noted that the EL spectra exhibit a shoulder peak in the range of 400–450 nm. As can be seen in Figure S11, SI, such a shoulder peak is missing in the solid-state PL spectrum of complex 1, indicating that it is not a characteristic emission of this material. Indeed, this shoulder peak is a characteristic emission of the host matrix and can be ascribed to the PVK:PBD exciplex excited state (formed at the interface between the LUMO of PBD and the HOMO of PVK-I, see Figure 6), according to the literature.^[40] [To avoid confusion, it should also be mentioned that the shoulder peak at 400-450 nm in the emission spectra in Figure 3 is due to scattering from the experimental setup and it is dissimilar to the shoulder peak observed in the same region in the EL spectra (Figure 4)]. Furthermore, unlike electroplex emission, it is well-known that the exciplex emission is not red-shifted upon increasing the driving voltage (or current density).^[41] For instance, as displayed in Figure 4b,

Device Fabrication

At the first attempt to realize solution-processed WOLEDs based on **1**, three devices with different doping concentrations of complex **1** (i.e. 3, 6, and 12 wt. %) were fabricated, hereafter called device A, B, and C, respectively. The structure of the devices was ITO/PEDOT:PSS (30 nm)/PVK-h (15 nm)/PVK-I:PBD:complex **1** (3, 6, and 12 wt. %) (30 nm)/BCP(10 nm)/Alq₃(40 nm)/Al (150 nm)/Ag (50 nm). Details concerning the fabrication process are given in the Supporting Information (SI). The chemical structures of the materials used in the OLEDs are also shown in Figure S12, SI. To fabricate the EML, complex **1** was doped into a co-host system consisting of poly (*N*-vinylcarbazole) (PVK-I) hole transporting and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD) electron transporting materials with a weight ratio of 30:70 (PVK:PBD), kept fixed in all the devices. PVK-h and PVK-I are respectively high and low-molecular weight PVK.

As shown in Figure 4a, the devices emitted a greenish-white electroluminescence (EL) light with a characteristic emission peak at 518 nm. This value is slightly blue-shifted compared with the PL spectra shown in Figure 3 and Figure S11, SI, most likely due to microcavity effects in the device structure.^[6d,38] In addition, the bandwidths of the EL spectra are narrower in comparison to the PL spectra which can also be attributed to the microcavity effect in the devices.^[39] It is noteworthy to mention that complex **1** emits a yellow light and the CIE (Commission Internationale de l'Éclairage) chromaticity coordinates (*x*,*y*) for the PL spectrum shown in Figure S11, SI, were calculated to be (0.40, 0.48). The CIE chromaticity coordinates for the



Figure 4. (a) The electroluminescence (EL) spectra of devices A, B, and C; (b) the EL spectra of device A at different current densities. No shift in the EL spectra in device A was observed at different bias current densities applied to the device. The Full Widths at Half Maximum (FWHM) of the EL spectra in devices A, B, and C are 79.9 nm, 72.4 nm, and 71.6 nm, respectively.









Figure 5. The energy level alignment of the components used in the device structure. The electron and hole injection pathways from the corresponding charge transport materials into the emissive layer and formation of excitons on complex **1** molecules are also shown. Formation of exciplexes at the interface between the LUMO of PBD and the HOMO of PVK-I is also shown by the dashed arrow.

the EL spectra of device A for various current densities do not show any significant variation with applied bias current, indicating that the above-mentioned shoulder peak is not due to formation of PVK:PBD electroplexes. Interestingly, the PVK:PBD exciplex emission covers the missing blue region in the solid-state PL spectrum of complex **1**, to achieve white emission.

Furthermore, emission from complex **1** overweighs the contribution of PVK:PBD exciplex emission, indicating that direct charge trapping on complex **1** molecules is highly favored in these devices. It can be clearly understood from the energy level alignment between the components (Figure 5) that injection of electrons and holes from the charge transport layers into complex **1**, and subsequently formation of excitons on complex **1** molecules, can take place very efficiently. Moreover, direct charge trapping on an emitter can be evidenced when a shift in the current density-voltage (J–V) curves is present by increasing the doping concentration.^[42] Obviously, such a shift is observed when looking at the J–V curves of the OLEDs, shown in Figure S13, SI.

The luminance efficiency vs. current density-voltage (LE-J) and power efficiency vs. voltage (PE-V) plots of the OLEDs are illustrated in Figure 6a and Figure 6b, respectively. The maximum LEs obtained for devices A, B, and C are 1.12, 1.03, and 0.49 cd/A, which correspond to the current densities at 9.7, 10, and 2.4 mA/cm², respectively. The maximum power efficiencies (PEs) of the WOLEDs were also measured to be 0.30, 0.25, and 0.13 lm/W for devices A, B, and C, respectively. Even though these LE and PE values are low in comparison to those reported for phosphoresce and TADF-based WOLEDs,^[20,43] they are comparable with the best values reported in the literature for thermally-processed fluorescent zinc(II)-based WOLEDs (0.12 to 2.1 cd/A for LE and 0.038 to 1.17 lm/W for PE).^[44] It is important to note that the gradual decrease in the device efficiency of devices B and C compared with device A is due to the fact that, as mentioned above, the turn-on voltages of these devices increase by increasing the doping concentration. This is obviously not in contradiction with the AIE behavior of complex **1**, as described earlier in Figure 3, where the PL emission enhances



Figure 6. (a) The luminance efficiency vs. current density (LE-J); (b) the power efficiency vs. voltage (PE-V) curves of devices A, B, and C.





with increasing the concentration. The luminance vs. voltage plots of the devices are also shown in Figure S14. The maximum luminance values for devices A, B, and C were obtained to be 91.1, 30.4, and 14.7 cd/m², respectively.

Conclusions

In summary, a new zinc(II) coordination complex of a benzamidine N-oxide (AMOX) ligand was synthesized and characterized. This compound displays AIE behaviour and it is the prototype of a new family of AIE materials based on the AMOX ligand platform, presently under development. Solution-processed white-green OLEDs using this complex as the dopant in the EMLs were successfully fabricated and characterized. Remarkably for a fluorescent zinc(II)-based OLED, the device containing 3 wt. % of the complex shows the best LE and PE values (1.12 cd/A and 0.30 lm/W) in comparison to the other devices containing higher concentrations of the complex. While these values are promising for the development of solution-processed single-compound WOLEDs based on Zn^{II} complexes exhibiting AIE behaviour, the structure of the devices should be optimized in order to enter into practical applications for the lighting technologies.^[43a-43c] Therefore, further studies on device structures are ongoing to improve the efficiencies of WOLEDs based on zinc(II) AMOX complexes. Additionally, the CIE chromaticity coordinates for all the devices are quite similar and exhibit the coordinates of a greenish-white light. By optimizing the device structure (for example, through device thickness variation), we believe that achieving color coordinates close to those of ideal white light would be possible. Overall, the characteristics of complex 1: high solubility, thermal stability, AIE behaviour, ease of synthesis, tunability options, and low-cost, already demonstrate great potential for development of this family of compounds for application in optoelectronic devices.

Experimental Section

Materials and Methods: Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ and/or [D₆]DMSO at room temperature (room temp.) (unless otherwise stated) on the following spectrometers: Bruker AV-400, AV-300, DRX-400, and ARX-300 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to TMS, using the residual solvent protons (δ =7.26 ppm and 2.50 ppm) as reference. Absorption spectra were measured in dichloromethane (DCM) (concentration range 10^{-4} – 10^{-6} M) at room temp. on a Cary 500i and a Cary 6000i UV/Vis-NIR Spectrophotometer. Luminescence spectra were obtained using a Perkin-Elmer LS55 Luminescence Spectrometer equipped with an accessory for measuring solid state samples. Excited state lifetime measurements were performed with an Edinburgh Instruments Miniature Fluorescence Lifetime Spectrometer (mini- τ). Quantum yield was determined for solid state samples (powder) by absolute method, using a FLSP920 Spectrometer (Edinburgh Instruments) equipped with an integrating sphere. Electrochemical measurements were carried out in argon-purged dry DCM at room temperature with a BAS CV50W potentiostat. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 0.46 V vs. SCE in DCM. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rate of 100 mV/s. For irreversible oxidation processes, the anodic peak was used as E. Thermogravimetric analyses (TGA) were carried out on a TGA2950 Thermogravimetric Analyzer (TA Instruments) under N2 atmosphere, in the 25-600 °C temperature range, at a heating rate of 10 °C/min. High-Resolution Mass Spectrometry (HRMS) analyses were performed on a Bruker micro-TOF II instrument by electrospray ionization (ESI) method for the ligand AMOX and using a cryosource (Bruker) for the complex 1. The microanalyses were done by the Elemental Analysis Service at Université de Montréal. Solvents, purchased from VWR and Fisher, were removed under reduced pressure using a rotary evaporator, unless otherwise stated. The m-CPBA from Acros Organics, P2O5, hexamethyldisiloxane (HMDS), 4-bromobenzoic acid, and metal salt, from Aldrich, were used without further purification. The aniline from Aldrich was distilled before use.

Details on the X-ray structure determination, X-ray powder diffraction measurements, computational studies and device fabrication are given in Supporting Information (SI).

Synthetic Details

4-Bromo-N,N'-diphenylbenzamidine (AM): The previously reported,^[22] amidine precursor was synthetized based on modified reported procedures.^[23,45]

4-Bromo-N,N'-diphenylbenzamidine N-Oxide (AMOX): To a solution of the corresponding amidine (1.50 g, 4.3 mmol, 1 equiv.) in DCM (100 mL), NaHCO₃ (0.39 g, 4.7 mmol, 1.1 equiv.) was added as a solid, followed by the slow addition at r. t. of a solution of m-CPBA (0.81 g, 4.7 mmol, 1.1 equiv.) in DCM (50 mL). The reaction mixture was stirred for 24 h, then was filtered and washed with an aqueous solution of NaOH 1M (2 \times 25 mL) and with water (2 \times 25 mL). The combined organic layers were dried with anhydrous MqSO₄ and filtered. After filtration and solvent evaporation, a brown solid was obtained, further purified by flash chromatography on silica [gradient of eluents: hexane/AcOEt (5:5), AcOEt 100 %, AcOEt/EtOH (9:1), EtOH 100 %]. The purification yielded a yellow solid, the desired product. Yield: 0.80 g, 51 %. m.p. 155-157 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (d, J = 8 Hz, 2 H), 7.27–7.21 (m, 5 H), 7.15 (t, J = 7 Hz, 2 H), 7.01 (t, J = 7 Hz, 1 H), 6.96 (d, J = 8 Hz, 2 H), 6.71 (d, J = 8 Hz, 1 H) ppm. ¹H NMR ([D₆]DMSO, 400 MHz): $\delta =$ 7.43 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 7.29 (t, J = 8 Hz, 2 H), 7.16–7.13 (m, 3 H), 7.08 (t, J = 8 Hz, 2 H), 6.84 (t, J = 7 Hz, 1 H), 6.64 (d, J = 8 Hz, 2 H) ppm. ¹³C NMR ([D₆]DMSO, 126 MHz): $\delta = 153.0$, 145.5, 144.1, 131.7 (2 C), 131.0 (2 C), 130.4, 128.4 (2 C), 128.3 (2 C), 125.7, 123.7 (2 C), 122.4, 122.1, 121.7 (2 C) ppm. MS (ESI, DCM) (*m/z*): 367.1 [M + H]⁺ (100 %). $C_{19}H_{15}BrN_2O$ (367.24): calcd. C 62.14, H 4.12, N 7.63; found C 61.95, H 3.73, N 7.54.

Bis[μ-(4-bromo-*N*,*N*'-diphenylbenzamidinate *N*-Oxide-κN,κO:κO)]bis[4-bromo-*N*,*N*'-diphenylbenzamidinate *N*-Oxide-κN,κO]dizinc-(II, II) (Complex 1): The synthesis of 1 was performed based on modified previously reported procedures.^[35,46] To a solution of the AMOX ligand (0.58 g, 1.6 mmol, 2 equiv.) in ethanol, aq. KOH was added to form a clear orange solution, which was then added to a solution of the metal salt Zn(AcO)₂·2H₂O (0.17 g, 0.79 mmol, 1 equiv.) in water, previously brought to pH 8 with aq. KOH. The total quantity of solvent used was 100 mL of EtOH 70 %. The formation of precipitate is observed almost instantly. The reaction mixture was stirred at room temperature for 24 h before water was added, and was kept at 4 °C for 2 h before being filtered. The resulted solid was washed with hot water and aqueous ethanol 50 %, and was





dissolved in DCM and dried with MgSO₄. A second filtration and evaporation of the solvent yielded the desired products as a pale beige-yellow-green solid, which was further recrystallized from DCM/hexane at -10 °C to yield the pure product as a pale yellow solid. 1 is very soluble in chlorinated solvents. X-ray quality crystals were obtained in DCM/hexane at -10 °C. Yield 0.44 g, 70 %. T_d (TGA, 5 % weight loss): 243 °C. ¹H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, J = 8 Hz, 2 H), 7.18–7.09 (m, 5 H), 7.05 (t, J = 8 Hz, 2 H), 6.90 (t, J = 7 Hz, 1 H), 6.82 (d, J = 8 Hz, 2 H), 6.67 (d, J = 7 Hz, 1 H) ppm. ¹³C NMR ([D₆]DMSO, 75 MHz): δ = 154.9, 147.6, 143.7, 132.2 (2 C), 131.1 (2 C), 130.9, 128.3 (2 C), 128.0 (2 C), 126.1, 126.0 (2 C), 124.8 (2 C), 122.2, 121.8 ppm. HRMS (Cryospray, DCM) (m/z): 1618.96243 [M + Na]+ (100 %), calcd. 1618.95732, error 3.2 ppm; 1596.97940 [M + H]⁺ (77 %) calcd. 1596.97538, error 2.5 ppm. $C_{76}H_{56}Br_4N_8O_4Zn_2$ (1595.71): calcd. C 57.21, H 3.54, N 7.02; found C 57.26, H 3.48, N 6.95.

Notes and references

CCDC 1531984 (for ####) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Optoelectronic Materials

 A Zinc(II) Benzamidinate N-Oxide
 Complex as an Aggregation-Induced Emission Material: toward Solution-Processable White Organic Light-Emitting Devices



 $Zn_2(AMOX)_4$ is a prototype for new AIE materials based on the amidine *N*-oxide ligand platform. Solution-processed white-green OLEDs were fabricated using it as the dopant in the emissive layer. The high solubility and thermal stability, together with AIE behaviour, ease of synthesis, tunability options, and low-cost demonstrate great potential for developing this family of compounds for optoelectronic applications.

Hanan and co-workers present a zinc complex suitable for an OLED which produces emission upon aggregation @UMontreal

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