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# Synthesis, structure and photophysical properties of 2-benzhydryl-4-methyl-6-(aryliminomethyl)phenol ligands and the zinc complexes thereof

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# ABSTRACT

The Schiff-base ligands 2-benzhydryl-4-methyl-6-((phenylimino)methyl)phenol (L1–L5), and their corresponding zinc complexes (C1–C5), were prepared and fully characterized. The UV–Vis absorption and fluorescence spectra of the ligands and their Zn(II) complexes were measured in solvents such as methanol, dichloromethane, THF, or toluene, respectively. The results showed that the fluorescence intensity of the ligands was very weak, but upon coordination with  $Zn^{2+}$ , the fluorescence intensity was greatly enhanced, and the fluorescent quantum yield ratio of C5 (0.46) to L5 (0.0004) in methanol increased by around 1150 times. The enhanced fluorescence of the zinc complexes is due to the intramolecular charge transfer (ICT) and the stronger geometrical rigidity of the delocalized bonding planes in these molecules. Transient absorption spectrum bands with peaks at about 310 and 460 nm were attributed to triplet state absorptions and absorption dynamic curve fitting showed that lifetimes were of microsecond level scale. There was no time-resolved property observed for the bleaching spectral bands at 350 nm and at ca. 460 nm. This spectral property, like the Stokes shift, can be attributed to the typical behavior of nanosecond transient absorption of the compounds with the excited-state intramolecular proton transfer (ESIPT).

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# 1. Introduction

Fluorescent sensors are an indispensable tool for visualizing or monitoring metal ions in real-time and real-space at a molecular level, and are of use in many fields such as medical diagnostics, environmental control, living cells, and electronics [1]. Zinc is an abundant component of most living cells [2], and plays important roles in various biological processes such as gene expression [3], regulation of metalloenzymes, neural signal transmission [4], and apoptosis [5]. Moreover, the zinc ion is also a contributory factor in neurological disorders such as epilepsy, Alzheimer's and Parkinson's diseases [1,6]. Consequently, research efforts on zinc-based organic materials with luminescent properties have been the focus of great interest for a number of decades.

As evidenced in the literature and by our previous studies, zinc complexes bearing bi- or tetra-dentate (*N*,*O*-donor atoms) Schiff base ligands have been extensively investigated. Zinc complexes have many advantages such as the combination of emitting and electron transferring roles, high environmental stability, little or

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no damage to the human body, and ease of preparation of the complexes [7-9]. The coordination modes of salicylaldehyde Schiff bases are similar to those of the 8-hydroxy-quinolines: such ligands have at least one hydroxyl group, a potentially coordinating nitrogen atom and a delocalized  $\pi$ -system. Metal-chelate complexes of salicylaldehyde Schiff base ligands tend to also exhibit good luminescent properties [10]. In addition, it has also been reported that a molecule possessing a C=N imine moiety generally has a high affinity for coordinating with metal ions such as zinc or cadmium ions [11]. Given this, we have designed a new type of Schiff base complex in which the ligands were synthesized from the reaction between salicylaldehyde derivatives possessing a bulky ortho substituent and an aniline (Scheme 1), and subsequently have investigated some photophysical properties of their neutral Zn(II) complexes. It was found in some cases that in the absence of Zn(II), the ligands exhibited almost no fluorescence emission, but the fluorescence intensity was largely enhanced after coordination with Zn(II) due to intramolecular charge transfer (ICT). ICT processes are, of course, highly desirable for this kind of molecular structure, and give large spectral shifts. Coordination with Zn(II) changes the electronic structure of the ligand, leading to the formation of a new extended  $\pi$ -conjugation system between ligand and Zn(II) [12-18].



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Scheme 1. Synthesis of ligands L1–L5 and complexes C1–C5.

#### 2. Results and discussion

#### 2.1. Molecular structures

The ligands were deprotonated with potassium hydride (KH) in THF at -78 °C, and the resultant potassium salts were reacted further with 0.5 equivalents of anhydrous ZnCl<sub>2</sub> in THF to afford glassy yellow products (Scheme 1). All complexes were characterized by elemental analysis and IR spectroscopy. Ligand **L4** and complexes **C2** and **C5** were further characterized by single-crystal X-ray crystallography (Figs. 1–3). The O(1)–C(1)–C(6)–C(7)–N(1) atoms of **L4** (Fig. 1) are almost coplanar, with the largest deviation from planarity being 0.0548 Å for O(1) and 0.0350 Å for N(1). In addition, the N atom deviates from the basal plane (C(1)–C(2)–C(3)) by 0.2074 Å (Fig. 1). The other important bond lengths and angles are listed in Table 1.

The selected bond lengths and angles of **C2** and **C5** are also listed in Table 1. The molecular structure of **C5** is shown in Fig. 2. Atoms N(1), O(1) and C(7) form the equatorial coordination plane, and the zinc center slightly deviates from the equatorial plane by 0.2060 Å. The two nitrogen atoms with the zinc core form an angle of 115.3(2)°, larger than the O(1)–Zn(1)–O(1A) bond angle 109.66(18)°. The Zn(1)–O(1) bond length is 1.926(3) Å, shorter than the Zn(1)–N(1) bond length 2.001(3) Å. Moreover, one coordination plane (O(1)–Zn(1)–N(1)) is approximately perpendicular to the other (O(1a)–Zn(1)–N(1a)) with a dihedral angle of 83.5°, and smaller than the corresponding value for **C2** (96.7°) (Fig. 3). In the solid-state structure of **C2**, the geometry at each zinc center can be best described as a distorted tetrahedron in which two chelating ligands are placed in a similar disposition about the metal center [7], but slight differences still occur. In particular, a longer



**Fig. 1.** Ortep plot of **L4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.



**Fig. 2.** Ortep plot of **C5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.



**Fig. 3.** Ortep plot of **C2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Zn(1)–O(1) bond length of 1.915(2) Å and a smaller dihedral angle (N(1)–C(7)–O(1) and N(1)–Zn(1)–O(1)) of 8.9° were observed for one ligand, while the respective values for the second ligand are 1.925(2) Å for Zn(1)–O(1a) and 9.7° for N(1a)–C(7a)–O(1a) and N(1a)–Zn(1)–O(1a). The Zn(1)–N(1)–O(1) plane and phenolate ring are almost coplanar with each other, forming a dihedral angle of 9.6°, which is smaller than the corresponding value for **C5** (10.7°). Moreover, the distance of the N atom (**C2** and **C5**, Figs. 3 and 2) from the C(1)–C(2)–C(3) ring is 0.0265 and 0.0054 Å, respectively, which is notably smaller than that of **L4** (0.2074 Å). The dihedral angles between the phenol ring (O(1)–C(1)–C(6)) and the aniline plane are notably different: 52.9° in **L4**, 75.9° in **C2**, and 104.3° in **C5**, these significant differences may be due to the steric effects of the other ligand present.

#### 2.2. UV-Vis absorption spectra in the organic solvents

The UV–Vis spectral data of the Zn complexes in different solvents are shown in Table 2. The absorption of the complexes

#### Table 1

	Selected bond lengths ()	Å) a	and angles (	°) for	complexes	L4,	C2	and	C5
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	L4	C2	C5
Bond lengths			
Zn(1) - O(1)		1.915(2)	1.926(3)
Zn(1)-O(1a)		1.925(2)	1.926(3)
Zn(1)-N(1)		2.003(3)	2.001(3)
Zn(1)-N(1a)		2.014(3)	2.001(3)
N(1)-C(7)	1.286(6)	1.301(4)	1.293(5)
N(1)-C(9)	1.419(5)	1.450(4)	1.451(5)
O(1)-C(1)	1.359(5)	1.313(4)	1.317(5)
C(6) - C(7)	1.466(6)	1.445(6)	1.442(6)
C(1) - C(6)	1.411(6)	1.422(5)	1.425(6)
C(1) - C(2)	1.399(6)	1.433(5)	1.431(6)
Bond angles			
O(1) - Zn(1) - O(1a)		110.40(10)	109.66(18)
O(1)-Zn(1)-N(1)		95.06(10)	96.36(13)
O(1a) - Zn(1) - N(1)		120.80(10)	120.36(13)
O(1) - Zn(1) - N(1a)		121.39(10)	120.36(13)
O(1a)-Zn(1)-N(1a)		95.49(10)	96.36(13)
N(1)-Zn(1)-N(1a)		115.58(10)	115.3(2)
O(1)-C(1)-C(6)	120.8(4)	123.8(3)	123.9(4)
C(6)-C(7)-N(1)	122.6(4)	127.7(3)	128.7(4)
C(7)-N(1)-C(9)	118.9(4)	117.3(3)	117.4(3)
C(1)-C(6)-C(7)	121.1(4)	124.6(4)	124.5(4)
O(1)-C(1)-C(2)	119.5(4)	118.5(3)	118.6(3)
C(2)-C(1)-C(6)	119.7(4)	117.5(3)	117.5(3)

#### Table 2

The spectral properties of ligands and Zn complexes in different solvents.

Solvent	Ligands	$\lambda_{abs-max} (nm)$	Complexes	$\lambda_{abs-max} (nm)$
Methanol	L1	342	C1	232
THF		346		237
Dichloromethane		344		294
Toluene		345		294
Methanol	L2	344	C2	216
THF		347		239
Dichloromethane		344		282
Toluene		346		293
Methanol	L3	343	C3	238
THF		345		265
Dichloromethane		346		279
Toluene		345		297
Methanol	L4	345	C4	215
THF		346		242
Dichloromethane		343		280
Toluene		349		294
Methanol	L5	344	C5	217
THF		346		263
Dichloromethane		343		281
Toluene		347		294

was very sensitive to the solvent. For example, in strongly polar solvents, the maximum absorption wavelengths of the complexes were blue-shifted compared to weakly polar solvents, and this indicated that the energy gap between the ground state and the excited state gradually became larger with the increase in solvent polarity. The absorption wavelengths of the Zn complexes (C1-C5) and the ligands (L1-L5) in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 4. According to Fig. 4(a), all complexes have two new absorption bands at about 410 and 236 nm, which can be assigned to ligand to metal charge transfer (LMCT) and a low-energy metal to ligand chargetransfer (MLCT,  $d \rightarrow \pi^*$  transition) [19], respectively. The two absorption bands around 347 and 280 nm associated with the corresponding ligands are shown in Fig. 4(b), and these absorption bands were shifted between 2 and 10 nm, consistent with internal charge transfer (ICT) within the ligand [16]. Shown in Fig. 4(b) for the ligands (L1–L5) in CH<sub>2</sub>Cl<sub>2</sub>, the narrow band at about 280 nm could be assigned to the  $n \rightarrow \sigma^*$  transition, whilst the intense broad band at about 347 nm could be assigned to the  $\pi \to \pi^*$  transition [20,21]. Similar red shifts were also observed in other solvents, however, there were no observed significant changes due to the influence of the substituents.

#### 2.3. Fluorescence properties of ligands and zinc complexes

The fluorescence properties of the Schiff base ligand and their zinc complexes were studied at room temperature (298 K) in methanol, THF, dichloromethane and toluene solution. The zinc complexes exhibited a number of interesting photophysical properties such as large Stokes shifts and enhanced luminescence intensity. As expected, **L1–L5** have very small fluorescent quantum yields, so much that they are almost too difficult to measure in our experiments. The large Stokes shifts, such as the emission bands for **L1** exhibited values of 198 nm in dichloromethane, 141 nm in methanol, 105 nm in THF, 204 nm in toluene, which belong to the ESIPT phenomenon (Table 3). A potential factor due to this phenomenon is an excited-state energy reduction of the keto tautomer after proton transfer, compared to that of excited enol configuration (Scheme 2).

Following coordination with Zn(II), the fluorescence emission spectrum was significantly blue shifted compared to corresponding ligands. Rate constants for radiative  $(k_r)$  and non-radiative  $(k_{\rm nr})$  decays of all complexes were calculated and are presented in Table 3. It is interesting to observe that all complexes (C1-C5) in methanol solution exhibited larger radiative decay rate constants (Table 3; k<sub>r</sub>; C1, C2, C3, C4, and C5 in methanol solution). Furthermore, complexes in methanol showed longer fluorescence lifetime than that observed when employing other solvents (see Table 3). This might be caused by the possible presence of dissolved oxygen in the methanol, which results in hydrogen bonds between the protic solvent and the zinc complexes, thereby strengthening the delocalization and the planarity/rigidity (Scheme 3) [22-24]. Regarding the observations in dichloromethane, which can often contain amounts of acid, the nitrogen atoms within the complex could be protonated and thereby be capable of forming further hydrogen bonding [25]. In general, all the zinc complexes showed stronger fluorescence than did the corresponding ligands and this can be understood in terms of the ring formed between zinc and the bi-dentate ligand, leading to a more rigid molecular skeleton.

The fluorescence intensity for the ligands and their zinc complexes in THF and toluene solutions are shown in Fig. 5, and it is evident that all complexes again exhibit strong fluorescence in comparison to the corresponding ligands. In the presence of the lone pairs of electrons of the donor atoms in the ligand, the fluorescence of the ligand was probably quenched by the occurrence of an ICT process or ESIPT [26-32]. A conceptually related system (L1-L5) contains the N<sup>O</sup> salicylaldimine, which deprotonates upon Zn(II) entry at the ligand to form a six-membered ring can significantly reduce the energy gaps between the  $\pi$  and  $\pi^*$  orbital, the HOMO and LUMO, as well as the orbitals with energies close to the HOMO and LUMO [33,34]. In addition, coordination with the Zn atom can enhance the rigidity of the ligand [12,35], which can diminish the loss of energy via vibrational motions and increase the emission efficiency, thereby resulting in further fluorescence enhancement [23,36].

#### 2.4. Transient absorption spectra and possible excited species

Fig. 6(a) and (b) shows the transient absorption spectra of **L5** in toluene solvent, conducted with and without de-oxygenation, respectively. Clearly, there are two prominent transient absorption bands with peaks at about 312 and 470 nm for the both deoxygenating and oxygenated system. The only spectral difference was that



Fig. 4. (a) UV–Vis absorption spectra of zinc complexes (C1–C5) in THF. Concentration:  $2 \times 10^{-4}$  M. (b) UV–Vis absorption spectra of ligands (L1–L5) in THF. Concentration:  $2 \times 10^{-4}$  M.

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Solvent	Ligar	nds			Complexes							
		$\lambda_{\max Em} (nm)$	$\lambda_{\mathrm{Ex}} \left( \mathrm{nm} \right)$	$\Delta\lambda^{a}(nm)$		$\lambda_{\max Em}$ (nm)	$\lambda_{\mathrm{Ex}} (\mathrm{nm})$	$\Delta\lambda^{a}(nm)$	τ (ns)	$\Phi_F$	$k_{\rm r}^{\rm b}$	k <sub>nr</sub> <sup>c</sup>
Methanol	L1	486	345	141	C1	489	340	146	5.748	0.08	13.92	1.601
THF		455	350	105		489	405	84	6.430	0.01	1.555	1.540
Dichloromethane		538	340	198		490	330	160	6.616	0.03	4.534	1.466
Toluene		549	345	204		495	410	85	6.253	0.03	4.798	1.551
Methanol	L2	436	345	91	C2	488	340	145	6.236	0.34	54.52	1.058
THF		536	345	191		488	405	83	6.277	0.01	1.593	1.577
Dichloromethane		547	340	207		489	340	149	6.686	0.06	8.974	1.406
Toluene		555	345	210		490	410	80	6.358	0.02	3.146	1.541
Methanol	L3	484	345	139	C3	486	340	143	6.072	0.26	42.82	1.219
THF		446	345	101		484	405	79	7.103	0.01	1.408	1.394
Dichloromethane		542	340	202		491	350	141	7.166	0.02	2.791	1.368
Toluene		546	345	201		491	410	81	6.974	0.03	4.302	1.391
Methanol	L4	437	345	92	C4	480	340	137	4.934	0.29	58.78	1.439
THF		480	350	130		486	405	81	5.530	0.01	1.808	1.790
Dichloromethane		543	340	203		487	347	140	4.915	0.05	10.17	1.933
Toluene		548	350	198		487	415	72	5.188	0.06	11.56	1.812
Methanol	L5	528	345	183	C5	485	340	142	5.100	0.46	90.20	1.059
THF		433	345	88		485	405	80	7.386	0.01	1.354	1.340
Dichloromethane		538	340	198		488	340	148	5.107	0.12	23.49	1.723
Toluene		547	350	197		488	415	73	5.452	0.05	9.171	1.742

<sup>a</sup>  $\Delta \lambda$  = Stokes shift.

Table 3

<sup>b</sup>  $k_{\rm r} = \Phi_F / \tau \ (10^6 \, {\rm s}^{-1}).$ 

<sup>c</sup>  $k_{\rm nr} = (1 - k_{\rm r} \cdot \tau)/\tau \ (10^8 \ {\rm s}^{-1}).$ 



Scheme 2. The excited-state energy reduction comparison between the keto tautomer and enol configuration.



Scheme 3. The plausible interaction between zinc complex and solvent methanol.

the spectral intensity of the deoxygenated sample was about 10% higher than that of the sample without de-oxygenation. Also there was a bleaching band with a peak at 350 nm. On recalling previous transient absorption spectra of some Schiff bases [37,38], the transient absorption spectra clearly were from their excited triplet state species due to similar spectrum bands. The experiments with and without deoxygenation also supported this assignment. That is, absorption decay curves of all samples with deoxygenation have longer exponential function fitting lifetimes due to the removal of oxygen as triple state quenching agent and some values are listed in Table 4. Here, one important point we should pay attention to is that the bleaching band was almost stable over time. In other words, the bleaching band differs from the positive transient absorption band by having a time-resolved feature. This seems to imply that the excited state species does not go back to the ground state (Scheme 2). However, the series of decay curves have shown that the excited state giving rise to the transient absorption signals indeed went back to the ground state. In regard to the bleaching bands without the time-resolution along with the absorption at about 460 nm, these may be attributed to the compounds with ESIPT phenomenon. In fact, so long as we recall that fluorescence properties with large Stoke shift are due to ESIPT, the fluorescence lifetimes of the compounds with the light-induced keto state are only about 0.6-1.0 ns (see Table 4) on average by employing the excited source of the 355 nm pulse-width laser. When the absorption excited state decays to zero, this means that the excited state can directly go back to the ground state (enol) and does not go back to the keto form. Therefore, this bleaching band has almost lost the time-resolved feature within the nanosecond (ns) scale. Up to now, experimental characterization of the ESIPT phenomenon has been made by their time-resolved fluorescence with a large Stokes shift as a feature. As far as we are aware, there is no evidence reported from corresponding transient absorption experiments in the literature. In the present work, we not only gave fluorescence experimental evidence, but also present the first transient absorption experimental evidence for the ESIPT phenomenon at ns scale. In

addition, the same measurements were done for **C5** and the absorption spectra showed similar results, when compared to **L5**.

# 3. Conclusions

A series of 2-benzhydryl-4-methyl-6-((phenylimino)methyl)phenol ligands L1–L5, and their Zn(II) complexes (C1–C5) were prepared and characterized. Molecular structures of L5, C2 and C5 were confirmed by single-crystal X-ray diffraction. The UV– Vis absorption and fluorescence spectral properties of ligands and their Zn(II) complexes were investigated. In strong polar solvents, the UV absorption wavelengths of the complexes were blue-shifted, whereas the fluorescence emission wavelengths of the complexes were red-shifted in lower polarity solvents. The fluorescence emission peaks of the ligands were very weak due to ICT or isomerization of the ligands, but when the zinc ion was bound by the chelating ligands (L1–L5) an ICT resulted in fluorescence enhancement.

#### 4. Experimental

#### 4.1. General considerations and materials

All manipulations of air and/or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. THF was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. ZnCl<sub>2</sub> was dried and refluxed over thionyl chloride. 3-Methyl-5-benzhydryl-6-hydroxy bentaldehyde was prepared according to the literature method [39]. All aniline derivatives were purchased from Aldrich or Acros Chemicals. Absorption spectra were determined on SHIMADZU UV-1601PC UV-Vis Spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DMX400 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer using KBr disc in the range of 400–4000 cm<sup>-1</sup>. Elemental analyses were performed on a Flash EA 1112 microanalyzer. The steady-state fluorescent spectra were measured on an F4500-FL fluorescence spectrophotometer; fluorescence lifetimes were obtained using the time-correlated single-photon counting technique (Edinburgh Analytical Instruments F900 fluorescence spectrofluorimeter). Thin films of the samples were prepared on quartz slides (1 cm) through spin-coating. Fluorescence quantum yields  $(\Phi_F)$  were calculated



**Fig. 5.** (a) Fluorescence spectra of the complexes **C1–C5** in THF, the inset shows the fluorescence spectra of the ligands **L1–L5** in THF. Concentration:  $7 \times 10^{-5}$  M. Excitation wavelength = 350 nm for **L1** and **L4**, 345 nm for **L2**, **L3** and **L5**, 405 nm for **C1**, **C2**, **C3** and **C4**, 400 nm for **C5**. (b) Fluorescence spectra of the complexes **C1–C5** in toluene, the inset shows the fluorescence spectra of ligands **L1–L5**. Concentration:  $7 \times 10^{-5}$  M. Excitation wavelength = 410 nm for **C1**, **C2** and **C3**, 415 nm for **C4** and **C5**, 345 nm for **L1**, **L2** and **L3**, 350 nm for **L4** and **L5**.



**Fig. 6.** Time-resolved transient absorption spectra of **L5** and **C5** in toluene solvent: (a) **L5** were deoxygenated for about 30 min by bubbling through the solution with high purity nitrogen gas (99.999%); (b) was the same sample (**L5**) without deoxygenation; (c) **C5** were deoxygenated for about 30 min by bubbling through the solution with high purity nitrogen gas (99.999%); and (d) was the same sample (**C5**) without deoxygenation. The inset shows the corresponding transient decays by exponential function fitting at 464 nm for (a), (b) and 448 nm for (c), (d). Concentration:  $5 \times 10^{-5}$  M.

Table 4

Exponential fitting vales of some decay curves.

Decay of sample	Fitting lifetimes (relative concentration)
L5 (deoxygenated) 464 nm	Single: 1027 µs; double:
	101.8 μs (2.7), 972.0 μs (97.3)
<b>L5</b> (air) 464 nm	Single: 703.6 µs; double:
	18.91 µs (2.1), 683.2 µs (97.9)
C5 (deoxygenated) 448 nm	934.4 µs
<b>C5</b> (air) 448 nm	845.1 µs
	•

according to the comparative method [7,40,41], using anthracene in THF ( $\Phi_F$  = 0.297) as a standard [42].

$$\Phi_{F,x} = \Phi_{F,s} \frac{\int i_{F,x}(v) dv \cdot (1 - 10^{-A_s}) \cdot (n_x)^2}{\int i_{F,s}(v) dv \cdot (1 - 10^{-A_s}) \cdot (n_s)^2}$$

where  $\Phi_{F,s}$  is the quantum yield of standard, integrals  $\int I_{F,x}(v)dv$  and  $\int I_{F,s}(v)dv$  are the areas under curves of the sample and standard,  $I_{F,s}(v)$  and  $I_{F,s}(v)$  are fluorescence intensities at wavelength for the sample and the standard, respectively.  $A_x$  and  $A_s$  are absorptions of the sample and standard,  $n_x$  and  $n_s$  are refractive indices of the solvents. The transient absorption spectra were obtained by the nanosecond laser flash photolysis technique, and the used instrument is a conventional LFP instrument set-up named as LP920 by

Edinburgh Instruments Ltd. (England, UK). A nanosecond Nd:YAG laser system was used for sample excitation (Surelite Continuum laser, pulse width 5–8 ns) and Xe-lamp with 450 W was used as probe light. The conversion of light to electricity was completed with the HAMAMATSU PMT R955. Laser light was inducted into a sample quartz cell ( $1 \text{ cm} \times 1 \text{ cm} \times 4 \text{ cm}$ ) by right angle direction with probe light on the plane of the optical stable, and finally the signals were recorded with a Tektronix digital 100 MHz TDS3012B oscilloscope. Here, 355 nm laser was used as exciting source for all flash photolysis measurements.

#### 4.2. Syntheses and characterization

## 4.2.1. 2-((2,6-Dimethylphenylimino)methyl)-6-benzhydryl-4methylphenol (**L1**)

2,6-Dimethylbenzenamine (0.40 g, 3.30 mmol) and bentaldehyde (1.00 g, 3.30 mmol) were refluxed in absolute ethyl alcohol (40 mL) in the presence of *p*-toluenesulfonic acid (0.15 g, 0.87 mmol) for 4 h. The reaction mixture was cooled to room temperature. After solvent evaporation, the crude product was purified by column chromatography on alumina with petroleum ether/ ethyl acetate (100/1 v/v) as eluent to afford the product as a yellow powder in 25.3% (0.34 g, 0.84 mmol) yield. Mp 148–149 °C, IR (KBr; cm<sup>-1</sup>): v 3025, 2916, 1622, 1585, 1493, 1448, 1361, 1265, 1192, 982, 752. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  13.14 (s, 1H), 8.27

Table 5
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Summary of crystallographic data for L4, C2 and C5.

Complex	L4	C2	C5
Empirical formula Formula weight Crystal system Space group Unit cell dimensions	C <sub>30</sub> H <sub>29</sub> NO 419.54 monoclinic P2(1)/n	C <sub>62</sub> H <sub>60</sub> N <sub>2</sub> O <sub>2</sub> Zn 930.49 triclinic <i>P</i> 1	C <sub>64</sub> H <sub>64</sub> N <sub>2</sub> O <sub>2</sub> Zn 958.54 orthorhombic <i>Pbcn</i>
a (Å)	8.6521(17)	12.433(3)	21.925(4)
$h(\dot{\mathbf{A}})$	26.552(5)	15.346(3)	16.424(3)
c (Å)	10.833(2)	15.863(3)	16.866(3)
$\alpha (°)  \beta (°)  \gamma (°)  V (Å3)$	90.00 111.14(3) 90.00 2321.0(8)	70.36(3) 70.72(3) 72.60(3) 2629.7(9)	90.00 90.00 90.00 6073(2)
Z	4	2	4
$D_{ m calc}  ({ m g}  { m cm}^{-3}) \ \mu  ({ m mm}^{-1}) \ T  ({ m K})$	1.201 0.072 173(2)	1.175 0.511 173(2)	1.048 0.444 173(2)
F(000)	896	984	2032
θ range (°) Number of reflections collected	1.53–25.36 14868	1.41-27.49 25893	1.55-25.00 39198
Number of unique reflections	4244	11993	5338
Goodness-of-fit (GOF) on F <sup>2</sup>	1.238	1.108	1.179
R indices (all data)	$R_1 = 0.1338$ $wR_2 = 0.2764$	$R_1 = 0.0852$ $wR_2 = 0.1918$	$R_1 = 0.0899$ $wR_2 = 0.2111$

(s, 1H), 7.32–6.84 (m, 15H), 6.06 (s, 1H), 2.23 (s, 3H), 2.16 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS):  $\delta$  18.7, 20.7, 49.0, 118.2, 124.9, 126.3, 127.5, 128.4, 128.5, 129.6, 130.8, 132.1, 135.0, 143.7, 148.4, 156.9, 166.9. *Anal.* Calc. for C<sub>29</sub>H<sub>27</sub>NO: C, 85.89; H, 6.71; N, 3.45. Found: C, 85.88; H, 6.95; N, 3.32%.

## 4.2.2. 2-((2,6-Diethylphenylimino)methyl)-6-benzhydryl-4methylphenol (**L2**)

Using the same procedure as for the synthesis of **L1**, 2,6diethylbenzenamine (1.02 g, 6.86 mmol) was used instead of 2, 6-dimethylbenzenamine, and reacted with 3-methyl-5-benzhydryl-6-hydroxy bentaldehyde (2.07 g, 6.86 mmol) and *p*-toluenesulfonic acid (0.31 g, 1.81 mmol) in absolute ethyl alcohol (100 mL). The yellow powder **L2** was isolated in 31.4% (0.92 g, 2.12 mmol) yield. Mp 158 °C–159 °C, IR (KBr; cm<sup>-1</sup>): v 3026, 2963, 1602, 1583, 1494, 1447, 1365, 1262, 1158, 988, 797. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  13.09 (s, 1H), 8.27 (s, 1H), 7.32– 7.02 (m, 15H), 7.01 (s, 1H), 6.85 (s, 1H), 6.07 (s, 1H), 2.47 (q, *J* = 7.50 Hz, 4H), 1.12 (t, *J* = 7.52 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS):  $\delta$  14.4, 20.2, 24.3, 48.4, 124.7, 125.7, 125.9, 127.0, 127.8, 129.0, 130.2, 131.5, 133.9, 134.4, 143.2, 156.3, 166.3. *Anal.* Calc. for C<sub>31</sub>H<sub>31</sub>NO: C, 85.87; H, 7.21; N, 3.23. Found: C, 85.62; H, 7.19; N, 3.27%.

## 4.2.3. 2-((2,6-Diisopropylphenylimino)methyl)-6-benzhydryl-4methylphenol (**L3**)

Using the above procedure as described for **L2**, 2,6-diisopropylbenzenamine (0.89 g, 5.03 mmol), 3-methyl-5-benzhydryl-6-hydroxy bentaldehyde (1.52 g, 5.03 mmol) and *p*-toluenesulfonic acid (0.23 g, 1.33 mmol) were refluxed in absolute ethyl alcohol (100 mL) for 3 h. **L3** was obtained as a yellow powder in 31.2% (0.72 g, 1.56 mmol) yield. Mp 178–179 °C, IR (KBr; cm<sup>-1</sup>): v 3023, 2962, 1601, 1586, 1494, 1457, 1360, 1260, 1182, 989, 795. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  13.08 (s, 1H), 8.24 (s, 1H), 7.32–6.82 (m, 13H), 6.80 (s, 1H), 6.08 (s, 1H), 3.01–2.91 (m, 2H), 2.24 (s, 3H), 1.16 (d, *J* = 6.84 Hz, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS):  $\delta$  20.7, 22.6, 23.8, 28.1, 48.9, 118.1, 122.9, 123.3, 125.4, 126.3, 127.6, 128.4, 129.6, 130.8, 132.1, 135.0, 139.0, 143.7, 146.5, 159.9, 166.8. *Anal.* Calc. for C<sub>33</sub>H<sub>35</sub>NO: C, 85.86; H, 7.64; N, 3.03. Found: C, 85.63; H, 7.34; N, 3.19%.

#### 4.2.4. 2-Benzhydryl-6-((mesitylimino)methyl)-4-methylphenol (L4)

Using the above procedure with 2,4,6-trimethylbenzenamine (0.78 g, 5.80 mmol), 3-methyl-5-benzhydryl-6-hydroxy bentalde-hyde (1.75 g, 5.80 mmol) and *p*-toluenesulfonic acid (0.26 g, 1.53 mmol) was added and refluxed for 3 h. **L4** was obtained as a yellow powder in 37.0% (0.90 g, 2.15 mmol) yield. Mp 152–153 °C, IR (KBr; cm<sup>-1</sup>): *v* 3027, 2916, 1620, 1591, 1493, 1446, 1361, 1262, 1204, 984, 764. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  13.26 (s, 1H), 8.26 (s, 1H), 7.31–7.00 (m, 10H), 6.89 (s, 1H), 6.84 (s, 1H), 6.83 (s, 1H), 6.06 (s, 1H), 2.28 (s, 3H), 2.22 (s, 3H), 2.14 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS):  $\delta$  18.1, 20.2, 20.3, 48.5, 117.7, 125.7, 126.9, 127.8, 128.5, 129.0, 130.1, 131.5, 133.8, 134.3, 143.2, 156.4, 166.3. *Anal.* Calc. for C<sub>30</sub>H<sub>29</sub>NO: C, 85.88; H, 6.97; N, 3.34. Found: C, 85.61; H, 6.93; N, 3.31%.

# 4.2.5. 2-((2,6-Diethyl-4-methylphenylimino)methyl)-6-benzhydryl-4methylphenol (**L5**)

Similarly, using 2,6-diethyl-4-methylbenzenamine (2.41 g, 14.80 mmol) in the reaction (3-methyl-5-benzhydryl-6-hydroxy bentaldehyde (4.46 g, 14.80 mmol), *p*-toluenesulfonic acid (0.67 g, 3.89 mmol)) gave the **L5** in 18.2% (1.19 g, 2.66 mmol) yield. Mp 121–122 °C, IR (KBr; cm<sup>-1</sup>): v 3024, 2970, 1620, 1594, 1494, 1396, 1263, 1203, 983, 758. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  13.20 (s, 1H), 8.26 (s, 1H), 7.32–7.17 (m, 10H), 7.01 (s, 1H), 6.92 (s, 2H), 6.85 (s, 1H), 6.07 (s, 1H), 2.48 (q, *J* = 7.51 Hz, 4H), 2.32 (s, 3H), 2.23 (s, 3H), 1.11 (t, *J* = 7.52 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS):  $\delta$  14.5, 20.2, 20.6, 24.3, 48.4, 117.6, 125.7, 126.7, 126.9, 127.8, 129.0, 130.2, 131.5, 133.8, 134.0, 134.3, 143.2, 156.4, 166.3. *Anal.* Calc. for C<sub>32</sub>H<sub>33</sub>NO: C, 85.87; H, 7.43; N, 3.13. Found: C, 85.12; H, 7.47; N, 3.06%.

# 4.2.6. Bis((2-((2,6-dimethylphenylimino)methyl)-6-benzhydryl-4methyl)phenoxy)zinc (**C1**)

To a THF solution (20 mL) of **L1** (0.19 g, 0.50 mmol) was added KH (0.020 g, 0.50 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred for additional 2 h, then ZnCl<sub>2</sub> (0.034 g, 0.25 mmol) was added. The resultant mixture was stirred for 12 h at room temperature. The residue, obtained by removing the solvent under vacuum, was dissolved in 20 mL toluene. The mixture was then filtered, and the filtrate was evaporated to dryness under reduced pressure to give complex **C1**, which was obtained as a glassy yellow solid in 61.3% (0.16 g, 0.18 mmol) yield. IR (KBr; cm<sup>-1</sup>): v 3025, 1597, 1588, 1536, 1433, 1395, 1259, 1193, 984, 765. *Anal.* Calc. for C<sub>58</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 79.67; H, 5.99; N, 3.20. Found: C, 79.54; H, 6.31; N, 3.23%.

## 4.2.7. Bis((2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4methyl)phenoxy)zinc (**C2**)

Using the same procedure for the synthesis of **C1**, 2-((2,6-diethylphenylimino)methyl)-6-benzhydryl-4-methylphenol (**L2**, 0.43 g, 1.00 mmol) and KH (0.040 g, 1.00 mmol) were dissolved in 20 mL THF solution and stirred for additional 2 h at room temperature, and ZnCl<sub>2</sub> (0.068 g, 0.50 mmol) was added and stirred for further 12 h. **C2** was obtained as a glassy yellow solid in 55.2% (0.26 g, 0.28 mmol) yield. IR (KBr; cm<sup>-1</sup>): v 3026, 1596, 1588, 1535, 1426, 1388, 1259, 1183, 983, 730. *Anal.* Calc. for C<sub>62</sub>H<sub>60</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 80.02; H, 6.50; N, 3.01. Found: C, 79.89; H, 6.72; N, 3.04%.

# 4.2.8. Bis((2-((2,6-diisopropylphenylimino)methyl)-6-benzhydryl-4methyl)phenoxy)zinc (**C3**)

Using the same procedure, 2-((2,6-diisopropylphenylimino) methyl)-6-benzhydryl-4-methylphenol (L3, 0.46 g, 1.00 mmol)

was reacted with KH (0.040 g, 1.00 mmol), and after 2 h, ZnCl<sub>2</sub> (0.068 g, 0.50 mmol) was added. **C3** was obtained as a glassy yellow solid in 61.1% (0.30 g, 0.30 mmol) yield. IR (KBr; cm<sup>-1</sup>):  $\nu$  3022, 1622, 1578, 1537, 1462, 1393, 1258, 1167, 988, 728. *Anal.* Calc. for C<sub>66</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 80.33; H, 6.95; N, 2.84. Found: C, 80.12; H, 7.19; N, 2.73%.

# 4.2.9. Bis((2-benzhydryl-6-((mesitylimino)methyl)-4methyl)phenoxy)zinc (**C4**)

Using the same procedure, 2-benzhydryl-6-((mesitylimino)methyl)-4-methylphenol (**L4**, 0.21 g, 0.50 mmol) was reacted with KH (0.034 g, 0.25 mmol) to form the phenolate, following which ZnCl<sub>2</sub> (0.034 g, 0.25 mmol) was added. The yellow solid of **C4** was obtained in 50.2% (0.11 g, 0.13 mmol) yield. IR (KBr; cm<sup>-1</sup>):  $\nu$  3023, 1617, 1589, 1536, 1438, 1390, 1260, 1167, 1021, 743. *Anal.* Calc. for C<sub>60</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 79.85; H, 6.25; N, 3.10. Found: C, 79.73; H, 6.48; N, 2.89%.

## 4.2.10. Bis((2-((2,6-diethyl-4-methylphenylimino)methyl)-6benzhydryl-4-methyl)phenoxy)zinc (**C5**)

Similarly, after 2-((2,6-diethyl-4-methylphenylimino)methyl)-6-benzhydryl-4-methylphenol (**L5**, 0.54 g, 1.20 mmol) was deprotonated by KH (0.048 g, 1.20 mmol) in toluene, ZnCl<sub>2</sub> (0.078 g, 0.58 mmol) was added; and the yellow solid of **C5** (0.42 g, 0.44 mmol, 73.4% yield) was obtained. IR (KBr; cm<sup>-1</sup>): v 3025, 1616, 1590, 1537, 1430, 1390, 1216, 1166, 986, 745. *Anal.* Calc. for C<sub>64</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 80.19; H, 6.73; N, 2.92. Found: C, 80.12; H, 7.07; N, 2.81%.

#### 4.3. X-ray crystallographic studies

Single crystals of complexes **C2** and **C5** suitable for X-ray diffraction were grown by the slow diffusion of *n*-heptane/ethyl ether into each THF solution, respectively. Single crystals of ligand **L4** were obtained by slow evaporation of THF. Crystallographic data of compounds **L4**, **C2**, and **C5** are summarized in Table 5. X-ray studies were carried out on a Rigaku Saturn724 + CCD with graphite-monochromatic Mo K $\alpha$  radiation (k = 0.71073 Å) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by fullmatrix least squares on  $F^2$ . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [43].

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#### Appendix A. Supplementary material

CCDC 851615, 851616, and 851617 contain the supplementary crystallographic data for **L4**, **C2** and **C5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.03.046.

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